


GAS-BARRIER RESIN COMPOSITION AND FILM**Publication number:** JP6093133**Publication date:** 1994-04-05**Inventor:** KOTANI KOZO; KAWAKITA TOSHIO; SAKATANI TAIICHI;
KURODA TOSHIYA**Applicant:** SUMITOMO CHEMICAL CO**Classification:****- International:** B32B27/28; C08J3/205; C08L101/02; B32B27/18; C08K3/00;
C08K3/34; C08K7/00; C08L29/04; C08L101/00; B32B27/28;
C08J3/20; C08L101/00; B32B27/18; C08K3/00; C08K7/00;
C08L29/00; (IPC1-7): C08K7/00; B32B27/28; C08K3/00;
C08K3/34; C08L29/04; C08L101/00**- European:** B32B27/18; C08K3/34B; C08K7/00**Application number:** JP19930178066 19930719**Priority number(s):** JP19920202339 19920729**Also published as:** EP0590263 (A2)
JP2005068441 (A)
JP2002201367 (A)
EP0590263 (A3)
CN1248588 (A)

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PURPOSE:To obtain a gas-barrier resin compsn. having high gas and water vapor barrier properties or a film made from the compsn. by compounding a specific inorg. layered compd. with a resin. **CONSTITUTION:**A gas-barrier resin compsn. is prepd. by compounding an inorg. layered compd. which has a particle size of 5µm or lower and an aspect ratio of 50-5,000, swells and cleaves in a solvent, and pref. is a swellable clay mineral (e.g. a synthetic tetrasilylic fluoromica) with a resin which is pref. a resin exhibiting strong hydrogen bonding, still pref. PVA or a polysaccharide, in a vol. ratio of the compd. to the resin of (5:95)-(90:10).

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(19)日本国特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平6-93133

(43)公開日 平成6年(1994)4月5日

(51)Int.Cl. ⁵	識別記号	庁内整理番号	FI	技術表示箇所
C 0 8 K 7/00	K C J	7242-4 J		
B 3 2 B 27/28	1 0 2	6122-4 F		
C 0 8 K 3/00	K A A	7242-4 J		
3/34	K A H	7242-4 J		
C 0 8 L 29/04	L G M	6904-4 J		

審査請求 未請求 請求項の数13(全 10 頁) 最終頁に続く

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(54)【発明の名称】 ガスバリア性樹脂組成物およびフィルム

(57)【要約】

【目的】ハイレベルの気体、水蒸気遮断性を有するガスバリアフィルムを提供することを目的とする。

【構成】 粒径が5 μ m以下、アスペクト比が50以上5000以下の無機層状化合物と樹脂を含む樹脂組成物およびフィルム。

【特許請求の範囲】

【請求項1】粒径が $5\mu\text{m}$ 以下、アスペクト比が50以上5000以下の無機層状化合物と樹脂を含むことを特徴とする樹脂組成物またはそれよりなるフィルム。

【請求項2】無機層状化合物が、溶媒に膨潤・へき開することを特徴とする請求項1記載の樹脂組成物またはそれよりなるフィルム。

【請求項3】無機層状化合物が、膨潤性をもつ粘土鉱物であることを特徴とする請求項2記載の樹脂組成物またはそれよりなるフィルム。

【請求項4】無機層状化合物のアスペクト比が、200～3000であることを特徴とする請求項1、2または3に記載の樹脂組成物或はそれよりなるフィルム。

【請求項5】（無機層状化合物／樹脂）の体積比が（5／95）～（90／10）の範囲であることを特徴とする請求項1～4のいずれか1項に記載の樹脂組成物またはそれよりなるフィルム。

【請求項6】樹脂が高水素結合性樹脂であることを特徴とする請求項1～5に記載の樹脂組成物またはフィルム。

【請求項7】高水素結合性樹脂が、樹脂単位重量当りの水素結合性基またはイオン性基の重量百分率が30％以上50％以下であることを特徴とする請求項6に記載の樹脂組成物またはフィルム。

【請求項8】高水素結合性樹脂が、ポリビニルアルコールまたは多糖類であることを特徴とする請求項6に記載の樹脂組成物またはフィルム。

【請求項9】無機層状化合物が溶媒に膨潤・へき開した状態で、樹脂または樹脂溶液中に分散させ、その状態を保ちながら、溶媒を系から除去することにより得られる請求項2～10のいずれか1項に記載の樹脂組成物またはそれよりなるフィルムの製造方法。

【請求項10】請求項1～7のいずれか1項に記載のフィルムを少なくとも1層有する積層フィルムまたは積層体。

【請求項11】2軸延伸ポリプロピレン、2軸延伸ナイロン、2軸延伸ポリエチレンテレフタレートから選ばれる少なくとも1層と、請求項1～7のいずれか1項に記載のフィルムを少なくとも1層とを有する積層フィルムまたは積層体。

【請求項12】厚み $1\mu\text{m}$ 当りの 31°C 、 $61\%\text{RH}$ 下での酸素透過度が $2\text{cc}/\text{m}^2\cdot\text{day}\cdot\text{atm}$ 以下であることを特徴とする請求項1～8に記載の樹脂組成物またはフィルム。

【請求項13】厚み $1\mu\text{m}$ 当りの 31°C 、 $61\%\text{RH}$ 下での酸素透過度が $0.2\text{cc}/\text{m}^2\cdot\text{day}\cdot\text{atm}$ 以下であることを特徴とする請求項1～8に記載の樹脂組成物またはフィルム。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、ガスバリアー性に優れた樹脂組成物、フィルムおよび積層体に関するものである。

【0002】

【従来の技術】包装に求められる機能は多岐にわたるが、内容物保護性としての各種ガスバリアー性は食品の保存性を左右する大切な性質であり、流通形態、包装技術の多様化、添加物規制、嗜好の変化などにより、その必要性はますます大きくなっている。そして、ガスバリアー性は一般プラスチック材料の弱点でもあった。食品の変質要因としては、酸素、光、熱、水分等があげられ、とりわけ酸素はその起因物質として重要である。バリアーは酸素を有効に遮断すると同時にガス充填や真空包装などの食品の変質を制御する手段にとってもなくてはならない材料であり、酸素ガスだけでなく各種のガス、有機溶剤蒸気、香気などのバリア機能を有することにより、防錆、防臭、昇華防止に利用でき、菓子袋、カツオパック、レトルトパウチ、炭酸ガス飲料容器等の食品、化粧品、農薬、医療等の多くの分野で利用されている。

【0003】熱可塑性樹脂よりなるフィルムの中で、特に配向されたポリプロピレン、ポリエステル、ポリアミド等のフィルムは、優れた力学的性質や、耐熱性、透明性などを有し広く包装材料として用いられている。しかし、これらのフィルムを食品包装用として用いる場合には、酸素やその他の気体の遮断性が不十分であるため、酸化劣化や好気性微生物による内容物の変質を招き易かったり、香気成分が透過してしまい、風味が失われたり、外界の水分で内容物が湿らされて口当りが悪くなったり、と種々の問題を生じがちなものである。そこで通常は他のガスバリアー性の良い膜層を積層するなどの方法がとられている場合が多い。

【0004】従来より、ガスバリアー性の小さい透明プラスチック素材も種々知られており、例えば、ポリビニルアルコールやエチレンビニルアルコール共重合体およびポリ塩化ビニリデン系樹脂からなるフィルム等があるものの、缶詰、瓶詰に用いられる金属やガラス素材は酸素透過度がほとんど零であるのに対して、これらプラスチック素材は未だ無視できない程度の酸素を透過するものである。

【0005】そのほか、ガスバリアー性発現の方法として、樹脂中への扁平形態の無機物の分散方法があり、例えば、①特開昭62-148532号公報には、1、6-ヘキサンポリカーボネートジオールを用いた濃度30%のポリウレタン樹脂溶液100重量部にマイカ微粉末25重量部、ジメチルホルムアミド60重量部よりなる塗工液組成物を離型性基材上に塗工、乾燥し、次いで基材上から剥離する製造方法が記載されている。また、②特開昭64-043554号公報には、エチレン／ビニルアルコール共重合体のメタノール水溶液に、平均長さ $7\mu\text{m}$ で、アスペクト比140のマイカを添加し、これを冷水中

に注入して沈殿させ、濾過、乾燥し、ペレットとし、次いでフィルムを得る方法が記載されている。さらに③特開平3-93542号公報には、シリル基含有変成ポリビニルアルコールと合成ヘクトライトとが重量比で50:50である塗工組成物を、二軸延伸ポリエチレンテレフタレート(OPE T)上に塗布し、乾燥させ、熱処理(130~150℃)する方法が記載されている。しかし、これら技術において得られるフィルムは、ガスバリアー性について、未だ充分なものではなく、必ずしも満足できるものとはいえない。

【0006】

【発明が解決しようとする課題】本発明は、ハイレベルの気体、水蒸気遮断性を有するガスバリアー性の成形品、フィルムを提供することを目的とするものである。

【0007】

【課題を解決するための手段】上記課題を解決するため鋭意検討した結果、無機層状化合物と樹脂からなる樹脂組成物およびそれからなるフィルムにおいて、無機層状化合物のアスペクト比を大きくすることにより著しく優れたガスバリアー性が発現されることを見だし、本発明に至った。

【0008】すなわち本発明は、粒径が5μm以下、アスペクト比が50以上5000以下の無機層状化合物と樹脂を含むことを特徴とする樹脂組成物およびそれよりなるフィルムに関するものである。

【0009】本発明に用いられる無機層状化合物とは、単位結晶層が互いに積み重なって層状構造を有している無機化合物であり、粒径が5μm以下、アスペクト比が50以上5000以下であるものならば特に限定されない。ガスバリアー性に関しては、アスペクト比が200~3000の範囲がより好ましい。アスペクト比が50未満であればガスバリアー性の発現が十分でなく、500より大きいものは技術的に難しく、経済的にも高価なものとなる。また、粒径が3μm以下であれば透明性が、より良好となりより好ましい。無機層状化合物の具体例としては、グラファイト、リン酸塩系誘導体型化合物(リン酸ジルコニウム系化合物)、カルコゲン化合物(IV族(Ti, Zr, Hf)、V族(V, Nb, Ta)およびVI族(Mo, W)のジカルコゲン化合物であり、式MX₂で表わされる。ここで、Xはカルコゲン(S, Se, Te)を示す。)、粘土系鉱物などをあげることができる。

【0010】樹脂組成物中での真の粒径測定はきわめて困難であるので、本発明で用いられる無機層状化合物の粒径は、溶媒中、動的光散乱法により求めた値である。動的光散乱法で用いた溶媒と同種の溶媒で十分に膨潤させて樹脂に複合させる場合、樹脂中での無機層状化合物の粒径は、溶媒中の粒径に近いと考えることができる。

【0011】本発明で用いられる無機層状化合物のアスペクト比(Z)とは、 $Z = L/a$ なる関係で示される。

[Lは、溶媒中、動的光散乱法により求めた粒径であり、aは、無機層状化合物の単位厚みである(単位厚みaは、粉末X線回折法などによって無機層状化合物単独の測定で決められる値である。)]。但し、 $Z = L/a$ に於いて、組成物の粉末X線回折から得られた面間隔dが存在し、 $a < d$ なる関係を満たす。ここで、d-aの値が組成物中の樹脂1本鎖の幅より大であることが必要である。Zは、樹脂組成物中の無機層状化合物の真のアスペクト比とは必ずしもいえないが、下記の理由から、かなり妥当性のあるものである。

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【0012】樹脂組成物中の無機層状化合物のアスペクト比は直接測定がきわめて困難である。組成物の粉末X線回折法で得られた面間隔d、と無機層状化合物単独の粉末X線回折測定で決められる単位厚みaの間に $a < d$ なる関係があり、d-aの値が組成物中の樹脂1本鎖の幅以上であれば、樹脂組成物中において、無機層状化合物の層間に樹脂が挿入されていることになり、よって無機層状化合物の厚みは単位厚みaとなっていることは明らかである。また、樹脂組成物中での真の粒径測定はきわめて困難であるが、動的光散乱法で用いた溶媒と同種の溶媒で十分に膨潤させて樹脂に複合させる場合を考えれば、樹脂中での無機層状化合物の粒径は溶媒中のそれとかなり近いと考えることができる(但し、動的光散乱法で求められる粒径Lは、無機層状化合物の長径L_{max}を越えることはないと考えられるから、真のアスペクト比L_{max}/aは、本発明でのアスペクト比の定義Zを下回ることは理論的には有り得ない。)。上記2点から、本発明のアスペクト比の定義は妥当性の比較的高いものと考えられる。本発明において、アスペクト比または粒径とは、上記で定義したアスペクト比、粒径を意味するものである。

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【0013】大きなアスペクト比を有する無機層状化合物としては、溶媒に膨潤・へき開する無機層状化合物が好ましく用いられる。これらの中でも膨潤性を持つ粘土鉱物が好ましく、粘土系鉱物はシリカの四面体層の上部に、アルミニウムやマグネシウム等を中心金属にした8面体層を有する2層構造よりなるタイプと、シリカの4面体層が、アルミニウムやマグネシウム等を中心金属にした8面体層を両側から挟んだ3層構造よりなるタイプに分類される。前者としてはカオリナイト族、アンチゴライト族等を挙げることができ、後者としては層間カチオンの数によってスメクタイト族、バーミキュライト族、マイカ族等を挙げることができる。具体的には、カオリナイト、ディッカイト、ナクライト、ハロイサイト、アンチゴライト、クリソタイル、パイロフィライト、モンモリロナイト、ヘクトライト、テトラシリリクマイカ、ナトリウムテニオライト、白雲母、マーガライト、タルク、バーミキュライト、金雲母、ザンソフィライト、緑泥石等をあげることができる。

【0014】本無機層状化合物を膨潤させる溶媒は、特

に限定されないが、例えば天然の膨潤性粘土鉱物の場合、水、メタノール、エタノール、プロパノール、イソプロパノール、エチレングリコール、ジエチレングリコール、等のアルコール類、ジメチルホルムアミド、ジメチルスルホキシド、アセトン等が挙げられ、水やメタノール等のアルコール類がより好ましい。

【0015】本発明において用いられる樹脂は、特に限定されないが、例えば、ポリビニルアルコール（PVA）、エチレンービニルアルコール共重合体（EVOH）、ポリ塩化ビニリデン（PVDC）、ポリアクリロニトリル（PAN）、多糖類、ポリアクリル酸およびそのエステル類などが挙げられる。

【0016】好ましい例としては、樹脂単位重量当りの水素結合性基またはイオン性基の重量百分率が20%～60%の割合を満足する高水素結合性樹脂があげられる。さらに好ましい例としては、高水素結合性樹脂の樹脂単位重量当りの水素結合性基またはイオン性基の重量百分率が30%～50%の割合を満足するものがあげられる。高水素結合性樹脂の水素結合性基としては水酸基、アミノ基、チオール基、カルボキシル基、スルホン酸基、燐酸基、などが挙げられ、イオン性基としてはカルボキシレート基、スルホン酸イオン基、燐酸イオン基、アンモニウム基、ホスホニウム基などが挙げられる。高水素結合性樹脂の水素結合性基またはイオン性基のうち、さらに好ましいものとしては、水酸基、アミノ基、カルボキシル基、スルホン酸基、カルボキシレート基、スルホン酸イオン基、アンモニウム基、などが挙げられる。

【0017】具体例としては、例えば、ポリビニルアルコール、ビニルアルコール分率が41モル%以上のエチレンービニルアルコール共重合体、ヒドロキシメチルセルロース、ヒドロキシエチルセルロース、カルボキシメチルセルロース、アミロース、アミロペクチン、プルラン、カードラン、ザンタン、キチン、キトサン、セルロース、プルラン、キトサンなどのような多糖類、ポリアクリル酸、ポリアクリル酸ナトリウム、ポリベンゼンスルホン酸、ポリベンゼンスルホン酸ナトリウム、ポリエチレンイミン、ポリアリルアミン、そのアンモニウム塩、ポリビニルチオール、ポリグリセリン、などが挙げられる。

【0018】高水素結合性樹脂のさらに好ましいものとしては、ポリビニルアルコール、多糖類があげられる。ここでいうポリビニルアルコールとは、酢酸ビニル重合体の酢酸エステル部分を加水分解（けん化）して得られるものであり、正確にはビニルアルコールと酢酸ビニルの共重合体となったものである。ここで、けん化の割合はモル百分率で70%以上が好ましく、特に85%以上のものがさらに好ましい。また、重合度は100以上5000以下が好ましい。

【0019】ここでいう多糖類とは、種々の単糖類の縮

重合によって生体系で合成される生体高分子であり、ここではそれらをもとに化学修飾したものも含まれる。たとえば、セルロースおよびヒドロキシメチルセルロース、ヒドロキシエチルセルロース、カルボキシメチルセルロースなどのセルロース誘導体、アミロース、アミロペクチン、プルラン、カードラン、ザンタン、キチン、キトサン、などが挙げられる。

【0020】本発明において用いられる無機層状化合物と樹脂との組成比（体積比）は、特に限定されないが、一般的には、（無機層状化合物／樹脂）の体積比が5/95～90/10の範囲であり、体積比が5/95～50/50の範囲であることがより好ましい。また、無機層状化合物の体積分率が5/95より小さい場合には、バリア性能が十分でなく、90/10より大きい場合には製膜性が良好ではない。

【0021】無機層状化合物と樹脂よりなる組成物の配合方法は、特に限定されないが、例えば、樹脂を溶解させた液と、無機層状化合物を予め膨潤・へき開させた分散液とを混合後、溶媒を除く方法、無機層状化合物を膨潤・へき開させた分散液を樹脂に添加し、溶媒を除く方法、また樹脂と無機層状化合物を熱混練する方法、などが挙げられる。とりわけ大きなアスペクト比を容易に得る方法として前二者が好ましく用いられる。

【0022】また、積層体の基材は、特に限定されず、樹脂、紙、アルミ箔、木材、布、不織布などの一般的な基材が挙げられる。基材として用いられる樹脂としては、ポリエチレン（低密度、高密度）、エチレンープロピレン共重合体、エチレンーブテン共重合体、エチレンーヘキセン共重合体、エチレンーオクテン共重合体、ポリプロピレン、エチレンー酢酸ビニル共重合体、エチレンーメチルメタクリレート共重合体、アイオノマー樹脂などのポリオレフィン系樹脂、ポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリエチレンナフタレートなどのポリエステル系樹脂、ナイロンー6、ナイロンー6,6、メタキシレンジアミンーアジピン酸縮重合体、ポリメチルメタクリルイミドなどのアミド系樹脂、ポリメチルメタクリレート、などのアクリル系樹脂、ポリスチレン、スチレンーアクリロニトリル共重合体、スチレンーアクリロニトリルーブタジエン共重合体、ポリアクリロニトリルなどのスチレン、アクリロニトリル系樹脂、トリ酢酸セルロース、ジ酢酸セルロースなどの疎水化セルロース系樹脂、ポリ塩化ビニル、ポリ塩化ビニリデン、ポリフッ化ビニリデン、テフロンなどのハロゲン含有樹脂、ポリビニルアルコール、エチレンービニルアルコール共重合体、セルロース誘導体などの水素結合性樹脂、ポリカーボネート樹脂、ポリサルホン樹脂、ポリエーテルサルホン樹脂、ポリエーテルエーテルケトン樹脂、ポリフェニレンオキシド樹脂、ポリメチレンオキシド樹脂、液晶樹脂などのエンジニアリングプラスチック系樹脂などがあげられる。

【0023】これらの中でフィルム形態での積層体に於

いて、外層としては、二軸延伸されたポリプロピレン、ポリエチレンテレフタレート、ナイロンやKコートと呼ばれるポリ塩化ビニリデンをコートした二軸延伸されたポリプロピレン、ポリエチレンテレフタレート、ナイロンなどが好ましく配され、内層には、一般にヒートシール性が良好であることから、ポリオレフィン系樹脂、たとえば、ポリエチレン（低密度、高密度）、エチレン-プロピレン共重合体、エチレン-ブテン共重合体、エチレン-ヘキセン共重合体、エチレン-オクテン共重合体、ポリプロピレン、エチレン-酢酸ビニル共重合体、エチレン-メチルメタクリレート共重合体などが好ましく用いられる。

【0024】基材に本発明の組成物を積層する方法としては、特に限定はされない。基材がたとえばフィルムやシートの場合には、組成物の塗工液を基材表面に塗布、乾燥、熱処理を行うコーティング方法や、組成物フィルムを後からラミネートする方法などが好ましい。コーティング方法としては、ダイレクトグラビア法やリバースグラビア法及びマイクログラビア法、2本ロールコートコート法、ボトムフィード3本リバースコート法等のロールコーティング法、及びドクターナイフ法やダイコート法、ディップコート法、バーコーティング法やこれらを組み合わせたコーティング法などの方法が挙げられる。

【0025】塗膜厚は、基材の種類および目的とするバリア性能により異なるが、乾燥厚みで10 μ m以下が好ましく、さらに1 μ m以下がより好ましい（1 μ m以下では積層体の透明性が著しく高いという長所も合わせもつため、透明性の必要な用途にはさらに好ましい。）。下限については特に制限はないが、効果的なガスバリア性効果を得るためには1nm以上であることが好ましい。

【0026】また、本発明の効果を損なわない範囲で、本樹脂組成物およびフィルムには、紫外線吸収剤、着色剤、酸化防止剤等のさまざまな添加剤を混合してもよい。本発明は、上で述べたフィルム層を少なくとも1層有する積層フィルム、積層体を含むものである。

【0027】

【発明の効果】本発明によれば、樹脂および無機層状化合物の混合系において、無機層状化合物の粒径が5 μ m以下、アスペクト比が50以上5000以下のものを用いることにより、これまでにないハイレベルの気体遮断性、水蒸気遮断性を有するガスバリアフィルムを得ることが可能となる。

【0028】実施例に記したように、無機層状化合物を含まない場合は同じ樹脂であっても、バリア性は本発明に比べ極めて劣っていることがわかる（例えば、実施例1と比較例1）。また、樹脂および無機層状化合物からなる組成物であっても、アスペクト比が約30の場合は、本発明の実施例に比べて100倍以上バリア性の劣

るものであることがわかる（例えば、比較例3と実施例1）。またアスペクト比が200程度を境にバリア性付与効果に大きな変化があり、アスペクト比が、約200以上ではさらなるバリア性向上が期待できるのである。

【0029】また、本発明は樹脂組成物としては、これまでの材料からは想像できないハイレベルのバリア性を有している。厚み1 μ m当りの酸素透過度が31℃、61%RHの条件下で、市販の樹脂で最も優れた酸素バリア性を持つエチレン-ビニルアルコール共重合体ですら15cc/m²・day・atmであるのに対し、本発明では、酸素透過度が2以下のものや、さらに優れたものでは0.2以下のものが得られる。本発明の樹脂組成物は、バリア性において、樹脂を大きく越え、金属やセラミックのバリア性に迫っていることから、バリア性の観点からアルミ箔やガラスなどの金属や無機材料を必須としている用途にも用いることができ、これまでのバリア性樹脂組成物の常識を打ち破る材料とすることができる（金属の不透明性やセラミックの脆さなどの弱点については、樹脂組成物である本発明がそれらより優れていることは言うまでもない。）。

【0030】すなわち、本発明の包装材料としての用途として、フィルムとしては味噌、鰹節、菓子、ラーメン、ハム・ソーセージ、テトラパックなどや、パックごはん、カレー、シチューなどなどのボイルやレトルト用食品に用いられ、ボトルとしてはマヨネーズなどのスクイズボトル、ジュース、醤油、ソース、食用油、などの用途に、トレイとしては、ヨーグルトやプリンのカップ、電子レンジ食品のトレイ、などに、さらには輸液パック、半導体包装、酸化性薬品包装、精密材料包装など医療、電子、化学、機械などの産業材料包装などに、様々な形状で広範な用途に用いられるものである。

【0031】

【実施例】以下、実施例により本発明を詳細に説明するが、本発明はこれらに限定されるものではない。

【0032】各種物性の測定方法を以下に記す。

【酸素透過度】酸素透過度測定装置（OX-TRAN 10/50A、MOCON社製）、温度31℃（調湿恒温槽21℃）で測定した（相対湿度は約61%を示した）。

【厚み測定】0.5 μ m以上はデジタル厚み計により測定した。0.5 μ m未満は重量分析法（一定面積のフィルムの重量測定値をその面積で除し、さらに組成物比重で除した。）または、本発明の組成物と基材の積層体の場合などは、元素分析法（積層体の特定無機元素分析値（組成物層由来）と無機層状化合物単独の特定元素分率の比から本発明の樹脂組成物層と基材の比を求める方法）によった。

【粒径測定】超微粒子粒度分析計（BI-90、ブルックヘブン社製）、温度25℃、水溶媒の条件で測定した。動的光散乱法による光子相関法から求めた中心径を粒径 \bar{L} とした。

〔アスペクト比計算〕X線回折装置(XD-5A、(株)島津製作所製)を用い、無機層状化合物単独と樹脂組成物の粉末法による回折測定を行った。これにより無機層状化合物の面間隔(単位厚み) a を求め、さらに樹脂組成物の回折測定から、無機層状化合物の面間隔が広がっている部分があることを確認した。上述の方法で求めた粒径 L をもちいて、アスペクト比 Z は、 $Z=L/a$ の式により決定した。

【0033】〔実施例1〕合成マイカ(テトラシリリクマイカ(Na-Ts);トピー工業(株)製)をイオン交換水(0.7 μ S/cm以下)に0.65wt%となるように分散させ、これを無機層状化合物分散液(A液)とする。当該合成マイカ(NA-TS)の粒径は977nm、粉末X線回折から得られる a 値は0.9557nmであり、アスペクト比 Z は1043である。また、ポリビニルアルコール(PVA210;(株)クラレ製、ケン化度;88.5%,重合度1000)をイオン交換水(0.7 μ S/cm以下)に0.325wt%となるように溶解させこれを樹脂溶液(B液)とする。A液とB液とをそれぞれの固形成分比(体積比)が無機層状化合物/樹脂=3/7となるように混合し、これを塗工液とした。厚さ76 μ mのトリアセチルセルロース(TAC)フィルム(フジタック;富士写真フィルム(株)製)の表面ケン化処理したものを基板として、この基板フィルム上に組成液を塗布し、室温で乾燥させることによりガスバリア性フィルムを得た。当該塗工層の乾燥厚みは0.87 μ mであった。この積層フィルムの31 $^{\circ}$ C、61%RHにおける酸素透過度は、0.092cc/m²/dayであった。これを乾燥塗工厚み1.0 μ mに換算すると、31 $^{\circ}$ C、61%RHにおける酸素透過度は、0.08cc/m²/dayとなり、ガスバリア性に優れたものであった。

【0034】〔実施例2〕B液の樹脂をヒドロキシエチルセルロース((株)和光純薬製)とした以外は実施例1と同様にしてガスバリア性フィルムを得、酸素透過度試験を行った。結果は第1表に示したとおりガスバリア性に優れたものであった。

【0035】〔実施例3〕塗工および乾燥をダイレクト・グラビアコーター(マルチコーターM-200;(株)平野テクシード製)ダイレクトグラビア塗工法:塗工速度1.7m/分、乾燥温度80 $^{\circ}$ C、4回重ね塗りを用いた以外は実施例1と同様にしてガスバリア性フィルムを得、酸素透過度試験を行った。結果は第1表に示したとおりガスバリア性に優れたものであった。

【0036】〔実施例4〕塗工および乾燥をダイレクト・グラビアコーター(マルチコーターM-200;(株)平野テクシード製)ダイレクトグラビア塗工法:塗工速度1.7m/分、乾燥温度80 $^{\circ}$ C、4回重ね塗りを用い、基材樹脂として二軸延伸ポリスチレン(OPS)フィルム(厚さ25 μ m,(株)旭化成製;TYPE(TH)C0,コロナ処理)を用いた以外は実施例1と同様にしてガスバ

リア性フィルムを得、酸素透過度試験を行った。結果は第1表に示したとおりガスバリア性に優れたものであった。

【0037】〔比較例1〕無機層状化合物分散液(A液)を用いず、ポリビニルアルコール(PVA210;(株)クラレ製、ケン化度;88.5%,重合度1000)をイオン交換水(0.7 μ S/cm以下)に1wt%となるように溶解させ、これを樹脂溶液(B液)とした以外は実施例1と同様にしてフィルムを得、酸素透過度試験を行った。結果は第1表に示したとおりガスバリア性に劣ったものであった。

【0038】〔比較例2〕無機層状化合物分散液(A液)を用いず、ヒドロキシエチルセルロース(HEC;(株)和光純薬工業製)をイオン交換水(0.7 μ S/cm以下)に2wt%となるように溶解させ、これを樹脂溶液(B液)とした以外は実施例1と同様にしてフィルムを得、酸素透過度試験を行った。結果は第1表に示したとおりガスバリア性の劣ったものであった。

【0039】〔比較例3〕A液として合成ヘクトライト(日本シリカ工業(株)製ラポナイトXLG;粒径35nm、 a 値約1nm(回折ピークがブロード)、アスペクト比約35)をイオン交換水(0.7 μ S/cm以下)に2wt%となるように分散させたものとB液としてポリビニルアルコール(PVA210;(株)クラレ製、ケン化度;88.5%,重合度1000)をイオン交換水(0.7 μ S/cm以下)に1wt%となるように溶解させたものを用いた以外は実施例1と同様にしてフィルムを得、酸素透過度試験を行った。結果は第1表に示したとおりガスバリア性の劣ったものであった。

【0040】〔比較例4〕樹脂溶液(B液)を用いない以外は実施例1と同様にしてフィルムを作製したが、積層フィルムから合成マイカの粉末が剥離し、フィルム表面に傷が目立ち、製膜性に劣るものであった。

【0041】〔比較例5〕トリアセチルセルロース(TAC)フィルム(厚さ76 μ m;フジタック;富士写真フィルム(株)製)においては、61%RHにおける酸素透過度は、第1表に示したとおりガスバリア性の著しく劣ったものであった。

【0042】〔比較例6〕二軸延伸ポリスチレン(OPS)フィルム(厚さ25 μ m,(株)旭化成製;TYPE(TH)C0,コロナ処理)においては、フィルムの31 $^{\circ}$ C、61%RHにおける酸素透過度は、第1表に示したとおりガスバリア性の著しく劣ったものであった。

【0043】〔実施例5~17〕無機層状化合物、樹脂、基材、無機層状化合物と樹脂の比をそれぞれ第2表に示した構成で、製膜してなるフィルムの酸素透過度を測定した。製膜方法は、実施例1の方法で塗工液(A液、B液濃度は各2wt%)を作製し、グラビアコーター(テストコーターNCR3-230、CAG150、CR3;康井精機(株)製:マイクログラビア塗工法、塗

工速度1~3m/分、乾燥温度60℃(入口側ヒーター)100℃(出口側ヒーター))により、基材に塗布、製膜した。結果は第2表のとおり優れたガスバリア性を示した。

【0044】〔比較例7~14〕無機層状化合物、樹脂、基材、無機層状化合物と樹脂の比をそれぞれ第2表*

*に示した構成で、実施例5~17と同様にして製膜してなるフィルムまたは基材単独の酸素透過度を測定した。結果は第2表のとおりガスバリア性の劣ったものであった。

【0045】

【表1】

第1表

	基材	組成物配合・構成				酸素透過度 (cc/m ² ・day・atm)			備考 (外観など)
		樹脂種類 B	無機層状 化合物の 種類 A	体積比 B/A	膜厚 (nm)	測定条件	測定値	厚み1μm 換算値	
実施例1	TAC76	PVA210	NaTs	7/3	870	31℃、61%RH	0.092	0.08	
実施例2	TAC76	HEC	NaTs	7/3	10000	31℃、61%RH	0.185	1.85	
実施例3	TAC76	PVA210	NaTs	7/3	28.4	31℃、61%RH	5.94	0.16	
実施例4	OPS25	PVA210	NaTs	7/3	24.3	31℃、61%RH	2.13	0.05	
比較例1	TAC76	PVA210	なし	10/0	2000	31℃、61%RH	240.6	481.2	
比較例2	TAC76	HEC	なし	10/0	10000	31℃、61%RH	1829	18290	
比較例3	TAC76	PVA210	3Fナット	7/3	3200	31℃、61%RH	4.72	15.1	
比較例4	TAC76	なし	NaTs	0/10	---	31℃、61%RH	---	---	割壊性不可
比較例5	TAC76	なし	なし	---	---	31℃、61%RH	833.3	---	基材フィルム
比較例6	OPS25	なし	なし	---	---	31℃、61%RH	10284	---	基材フィルム

【0046】

【表2】

第2表

	基材	組成物配合・構成				酸素透過度 (cc/m ² ·day·atm)		
		樹脂種類	無機層状 化合物の 種類	体積比	膜厚 (nm)	測定条件	測定値	厚み1μm 換算値
実施例5	OPET25	PVA117H	ケニト [®] 7F	9/1	348	31℃, 61%RH	0.17	0.06
実施例6	OPET25	PVA117H	ケニト [®] 7F	8/2	554	31℃, 61%RH	0.05	0.027
実施例7	OPET25	PVA117H	ケニト [®] 7F	7/3	587	31℃, 61%RH	<0.05	<0.028
実施例8	OPET25	PVA117H	ケニト [®] 7F	5/5	594	31℃, 61%RH	0.05	0.028
実施例9	OPET25	PVA110	スメクト [®] SA	7/3	440	23℃, 78%RH	2.88	1.28
実施例10	OPET25	PVA110	NaTs	7/3	120	23℃, 78%RH	0.92	0.11
実施例11	OPET12	PVA103	スメクト [®] SA	8/2	375	31℃, 61%RH	1.32	0.495
実施例12	OPET12	PVA103	ケニト [®] 7F	8/2	335	31℃, 61%RH	0.20	0.067
実施例13	OPET12	PVA124	ケニト [®] 7F	8/2	525	31℃, 61%RH	0.24	0.13
実施例14	ONy15	PVA117H	ケニト [®] 7F	7/3	768	31℃, 61%RH	<0.05	<0.038
実施例15	OPP20	PVA117H	ケニト [®] 7F	8/2	188	31℃, 61%RH	0.33	0.06
実施例16	OPP20	PVA117H	ケニト [®] 7F	8/2	506	31℃, 61%RH	0.06	0.03
実施例17	OPP20	PVA117H	ケニト [®] 7F	8/2	506	24℃, 94.5%RH	0.16	0.08

【0047】

【表3】

第2表の2

	基材	組成物配合・構成				酸素透過度 (cc/m ² ·day·atm)			備考 (外観など)
		樹脂種類 B	無機層状 化合物の 種類 A	体積比 B/A	膜厚 (nm)	測定条件	測定値	厚み1μm 換算値	
比較例7	OPET12	PVA103	ナリ	B/2	382	31℃, 61%RH	4.48	9.62	
比較例8	OPET12	PVA124	なし	なし	1104	31℃, 61%RH	2.12	2.34	
比較例9	OPET25	PVA110	なし	なし	520	23℃, 78%RH	11.69	6.07	
比較例10	ONy15	PVA117H	なし	なし	1450	31℃, 61%RH	2.74	3.97	
比較例11	DPET12	なし	なし	なし	---	31℃, 61%RH	155.6	---	基材フィルム
比較例12	DPET25	なし	なし	なし	---	31℃, 61%RH	74.7	---	基材フィルム
比較例13	ONy15	なし	なし	なし	---	31℃, 61%RH	50.6	---	基材フィルム
比較例14	OPP20	なし	なし	なし	---	20℃, 0%RH	1500	---	基材フィルム

【0048】基材

(1) TAC76: トリアセチルセルロース (商品名フジタッククリア: 富士写真フィルム製) 表面ケン化品、膜厚76μm。

(2) OPS25: 2軸延伸ポリスチレン (商品名スタイルフィルム (TH) CO: 旭化成 製) 片面コロナ処理品、膜厚25μm。

(3) OPET25: 2軸延伸ポリエチレンテレフタレート (商品名ルミラー: 東レ 製) 片面コロナ処理品、膜厚25μm。

(4) OPET12: 2軸延伸ポリエチレンテレフタレート (商品名ルミラー: 東レ 製) 片面コロナ処理品、

膜厚12μm。

(5) ONy15: 2軸延伸ナイロン (商品名エンブレムON: ユニチカ 製) 片面コロナ処理品、膜厚15μm。

(6) OPP20: 2軸延伸ポリプロピレン (商品名パイレックスフィルム-OT: 東洋紡 製) 片面コロナ処理品、膜厚20μm。

【0049】樹脂

(1) PVA210: ポリビニルアルコール (商品名パール210: クラレ製) ケン化度88.5モル%、重合度1000。

(2) HEC: ヒドロキシエチルセルロース (和光純

薬製)

(3) PVA117H: ポリビニルアルコール (商品名ポパール117H: クラレ製) ケン化度99.6モル%、重合度1700。

(4) PVA110: ポリビニルアルコール (商品名ポパール110: クラレ製) ケン化度98.5%、重合度1000。

(5) PVA103: ポリビニルアルコール (商品名ポパール103: クラレ製) ケン化度98.5%、重合度300。

(6) PVA124: ポリビニルアルコール (商品名ポパール124: クラレ製) ケン化度98.5%、重合度2400。

【0050】無機層状化合物

10

*

* (1) NaTs: 合成テトラシリリックフッ化マイカ (商品名NaTs: トピー工業 製) 粒径977nm、a値0.9557nm、アスペクト比1043。

(2) ラポナイト: 合成ヘクトライト (商品名ラポナイト XLG: 日本シリカ工業 製) 粒径35nm、a値約1nm (回折ピークブロード)、アスペクト比約35。

(3) クニピアF: 高純度モンモリロナイト (商品名クニピアF: クニミネ工業製) 粒径560nm、a値1.2156nm、アスペクト比461。

(4) スメクトンSA: 合成サポナイト (商品名スメクトンSA: クニミネ工業製) 粒径108nm、a値約1nm (回折ピークブロード)、アスペクト比約108。

フロントページの続き

(51)Int.Cl.⁵

C08L 101/00

識別記号

庁内整理番号

7242-4J

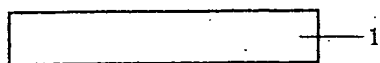
FI

技術表示箇所

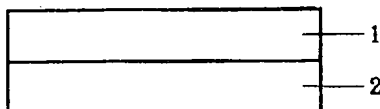
(72)発明者 黒田 俊也

大阪府高槻市塚原2丁目10番1号 住友化学工業株式会社内

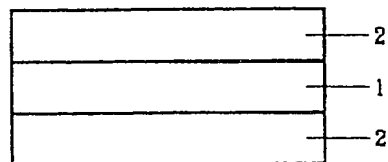
【図1】



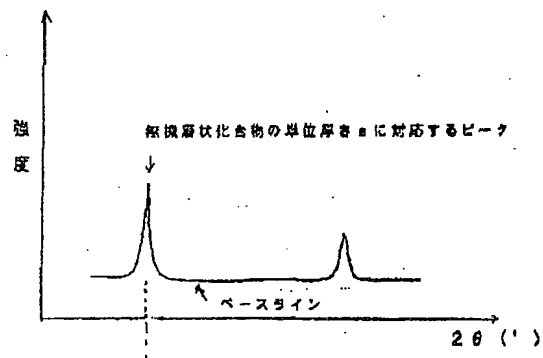
【図2】



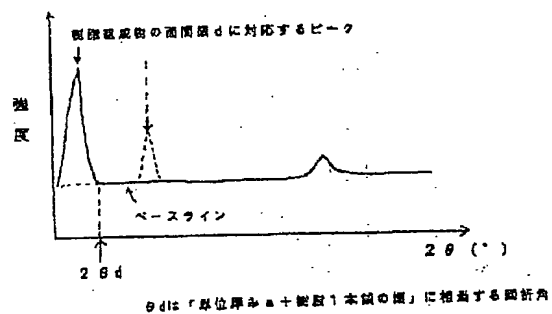
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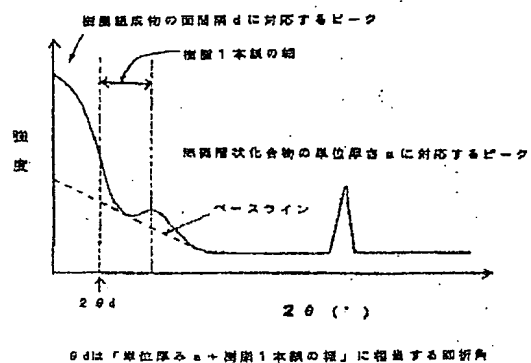
【図4】



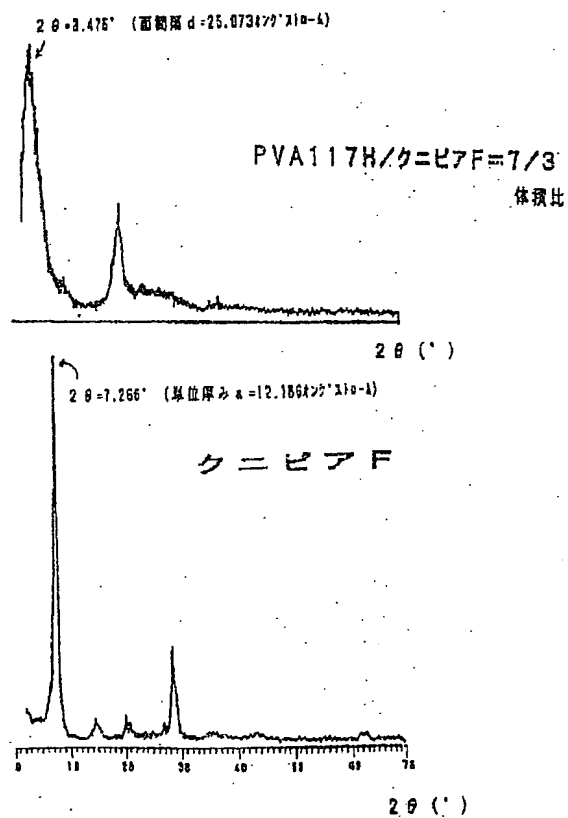
【図5】



【図6】



【図7】



Family list

22 family members for: JP6093133

Derived from 14 applications

[Back to JP6093133](#)

- 1 Gas barrier resin composition and its film and process for producing the same
Publication info: AU662429B B2 - 1995-08-31
AU4200693 A - 1994-02-03
- 2 GAS BARRIER RESIN COMPOSITION AND ITS FILM AND PROCESS FOR PRODUCING THE SAME
Publication info: CA2101037 A1 - 1994-01-30
- 3 Gas barrier resin composition and its film and process for producing the same
Publication info: CN1082071 A - 1994-02-16
- 4 Gas barrier resin composition and film thereof, and preparation process
Publication info: CN1136254C C - 2004-01-28
CN1248587 A - 2000-03-29
- 5 Gas barrier resin composition and film thereof, and preparation process
Publication info: CN1139623C C - 2004-02-25
CN1248588 A - 2000-03-29
- 6 No title available
Publication info: DE69333048D D1 - 2003-07-24
- 7 Gas barrier resin composition and process for producing the same.
Publication info: DE69333048T T2 - 2004-04-01
- 8 Gas barrier resin composition and process for producing the same.
Publication info: EP0590263 A2 - 1994-04-06
EP0590263 A3 - 1994-05-25
EP0590263 B1 - 2003-06-18
- 9 GAS-BARRIER RESIN COMPOSITION AND FILM
Publication info: JP3817274B2 B2 - 2006-09-06
JP6093133 A - 1994-04-05
- 10 GAS BARRIER RESIN COMPOSITION
Publication info: JP4004279B2 B2 - 2007-11-07
JP2002201367 A - 2002-07-19
- 11 GAS BARRIER RESIN COMPOSITION
Publication info: JP4042740B2 B2 - 2008-02-06
JP2005068441 A - 2005-03-17
- 12 GAS BARRIER RESIN COMPOSITION AND FILM AND PREPARATION THEREOF
Publication info: KR100312876B B1 - 2001-10-15
- 13 Gas barrier resin composition and its film and process for producing the same
Publication info: US5700560 A - 1997-12-23
- 14 Process for producing a gas barrier resin composition
Publication info: US5969029 A - 1999-10-19

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US005700560A

United States Patent [19]

Kotani et al.

[11] Patent Number: **5,700,560**[45] Date of Patent: **Dec. 23, 1997**[54] **GAS BARRIER RESIN COMPOSITION AND ITS FILM AND PROCESS FOR PRODUCING THE SAME**[75] Inventors: **Kozo Kotani, Toyonaka; Toshio Kawakita, Ibaraki; Taiichi Sakaya; Toshiya Kuroda, both of Takatsuki, all of Japan**[73] Assignee: **Sumitomo Chemical Company, Limited, Osaka, Japan**[21] Appl. No.: **416,380**[22] Filed: **Apr. 4, 1995****Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 384,798, Feb. 6, 1995, abandoned, which is a continuation of Ser. No. 97,889, Jul. 28, 1993, abandoned.

[30] **Foreign Application Priority Data**

Jul. 29, 1992 [JP] Japan 4-202339

[51] Int. Cl.⁶ **B32B 5/16**[52] U.S. Cl. **428/325; 428/331; 524/445; 524/447**[58] Field of Search **428/323, 325, 428/331; 524/442, 445, 447**[56] **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—H. Thi Le*Attorney, Agent, or Firm*—Cushman Darby & Cushman IP Group of Pillsbury Madison & Sutro, LLP[57] **ABSTRACT**

A gas barrier resin composition or its film having very high level gas barrier and moisture barrier properties, which includes at least a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound having a particle size of 5 μ m and an aspect ratio of 50-5,000. The resin composition or its film can be produced by dispersing a non-film-forming inorganic laminar compound in a high hydrogen-bonding resin or resin solution in such a state that the non-film-forming inorganic laminar compound is swollen or cloven with a solvent, and removing the solvent from the dispersion, if necessary in the form of a film, while maintaining the state.

18 Claims, 7 Drawing Sheets

FIG. 1

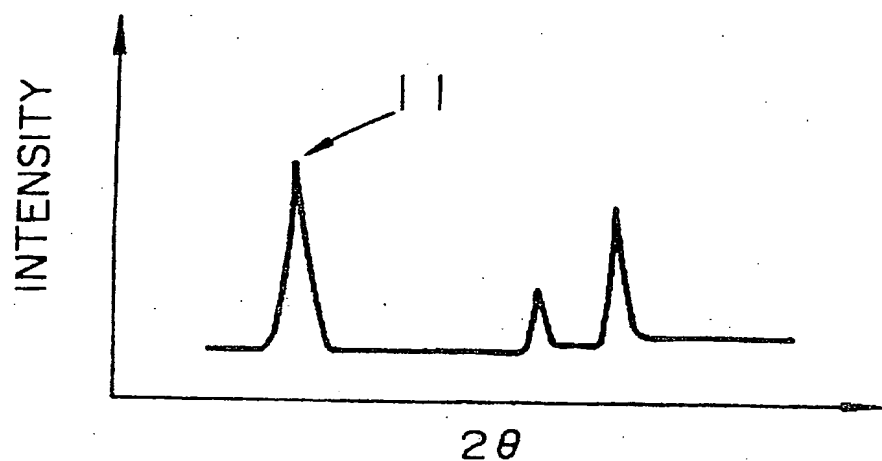


FIG. 2

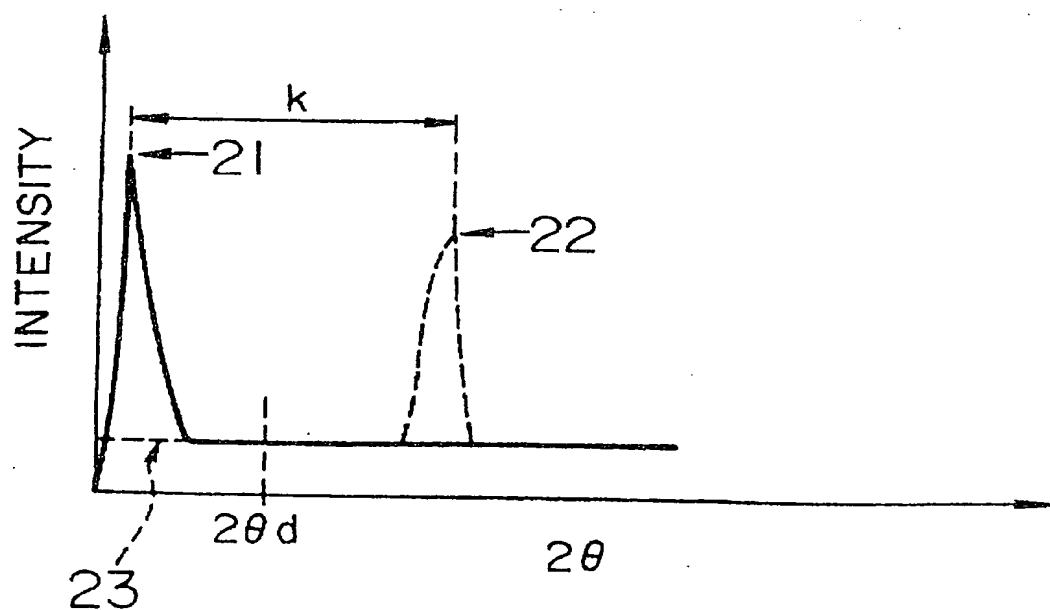


FIG. 3

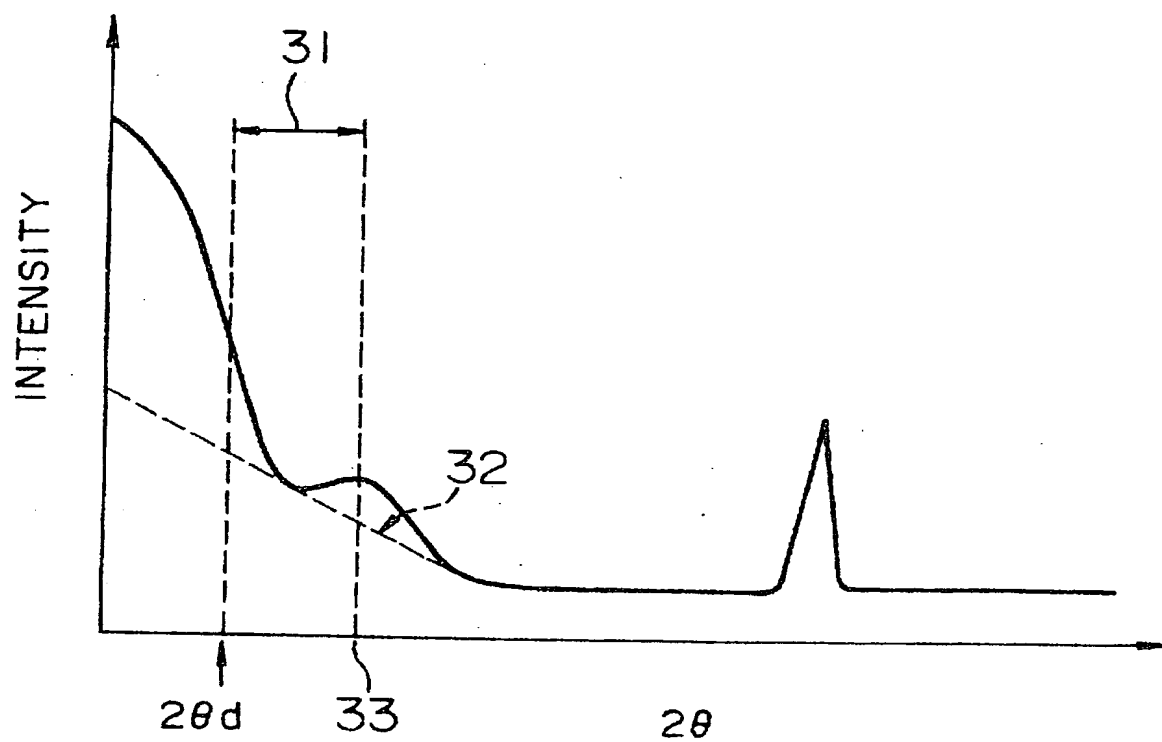


FIG. 4

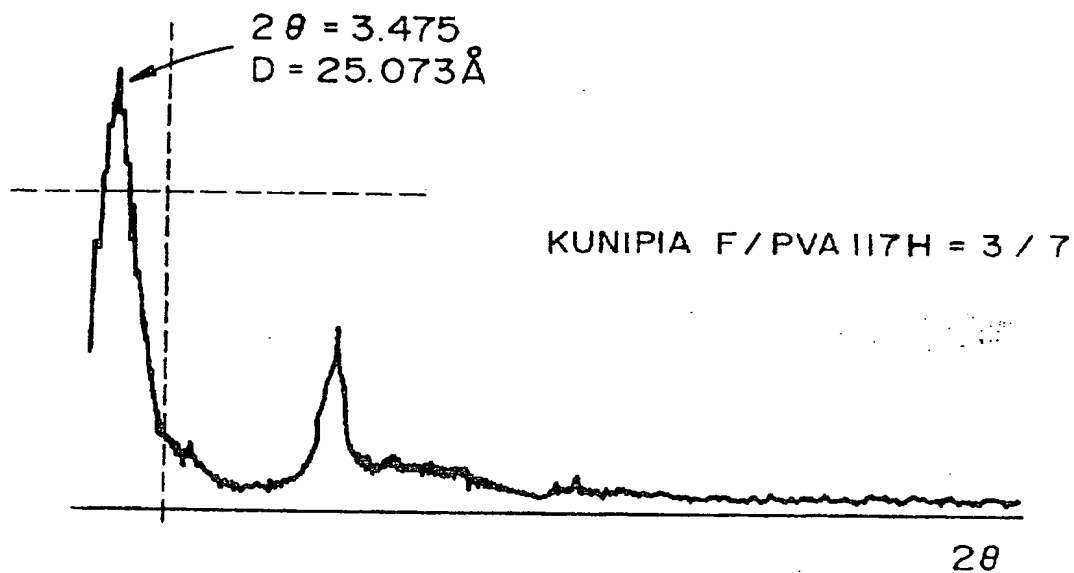


FIG. 5

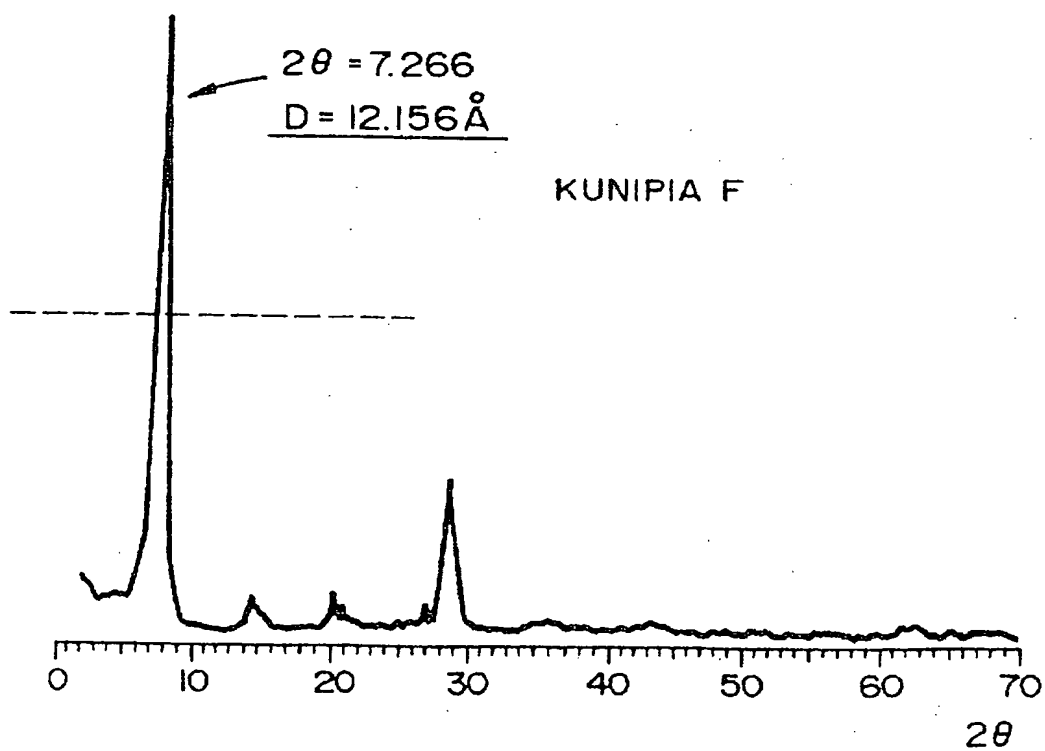


FIG. 6

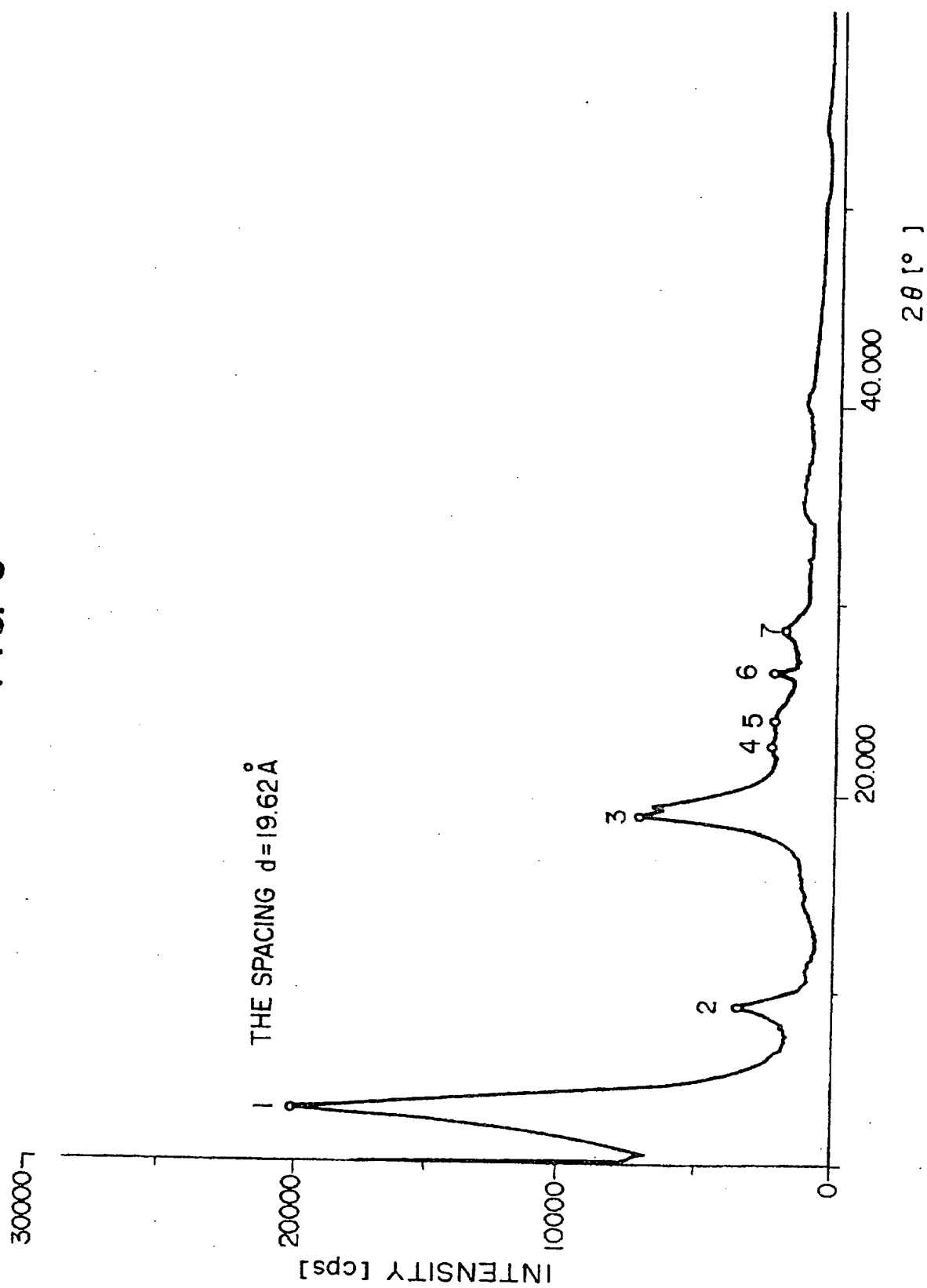


FIG. 7

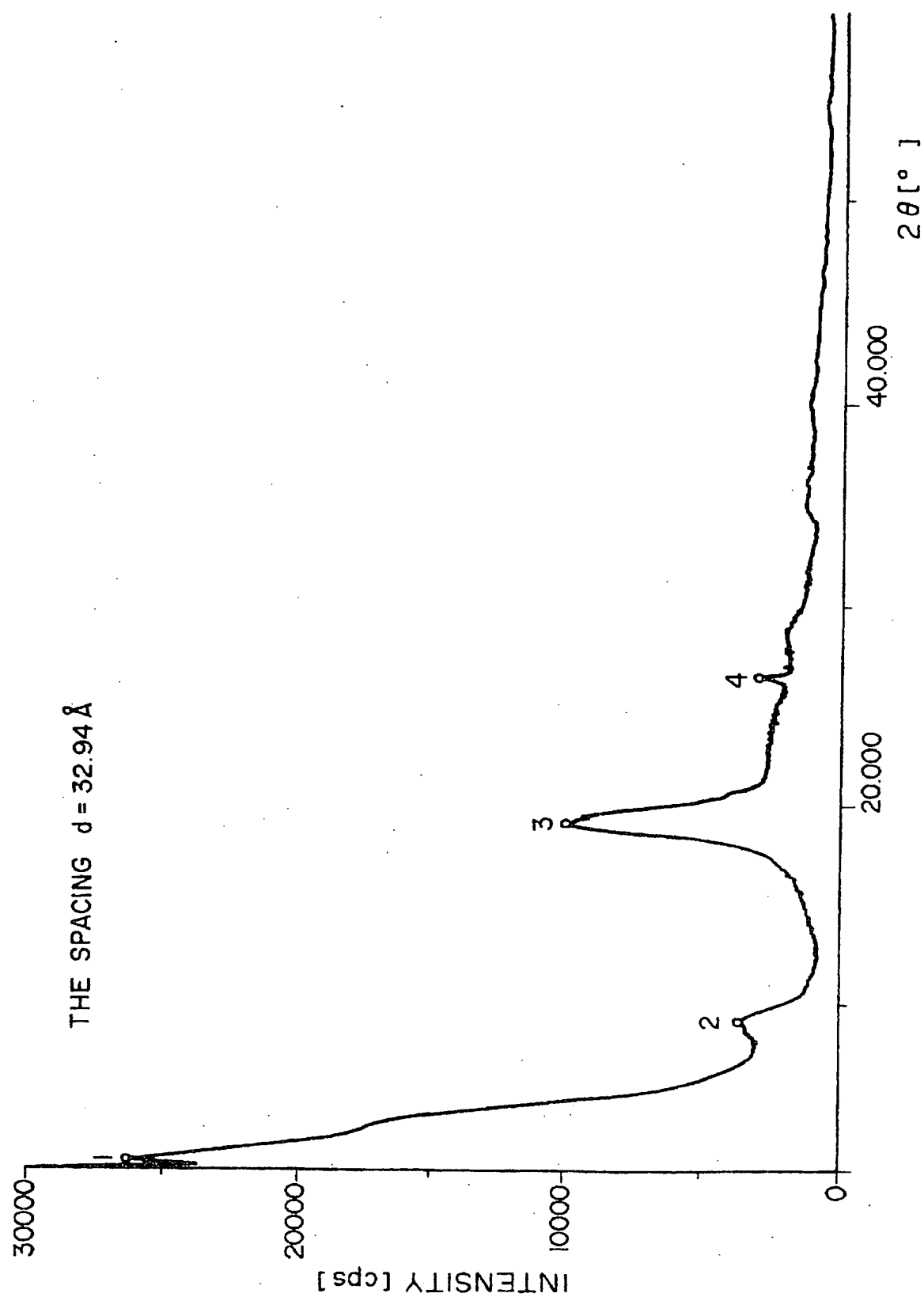


FIG. 8

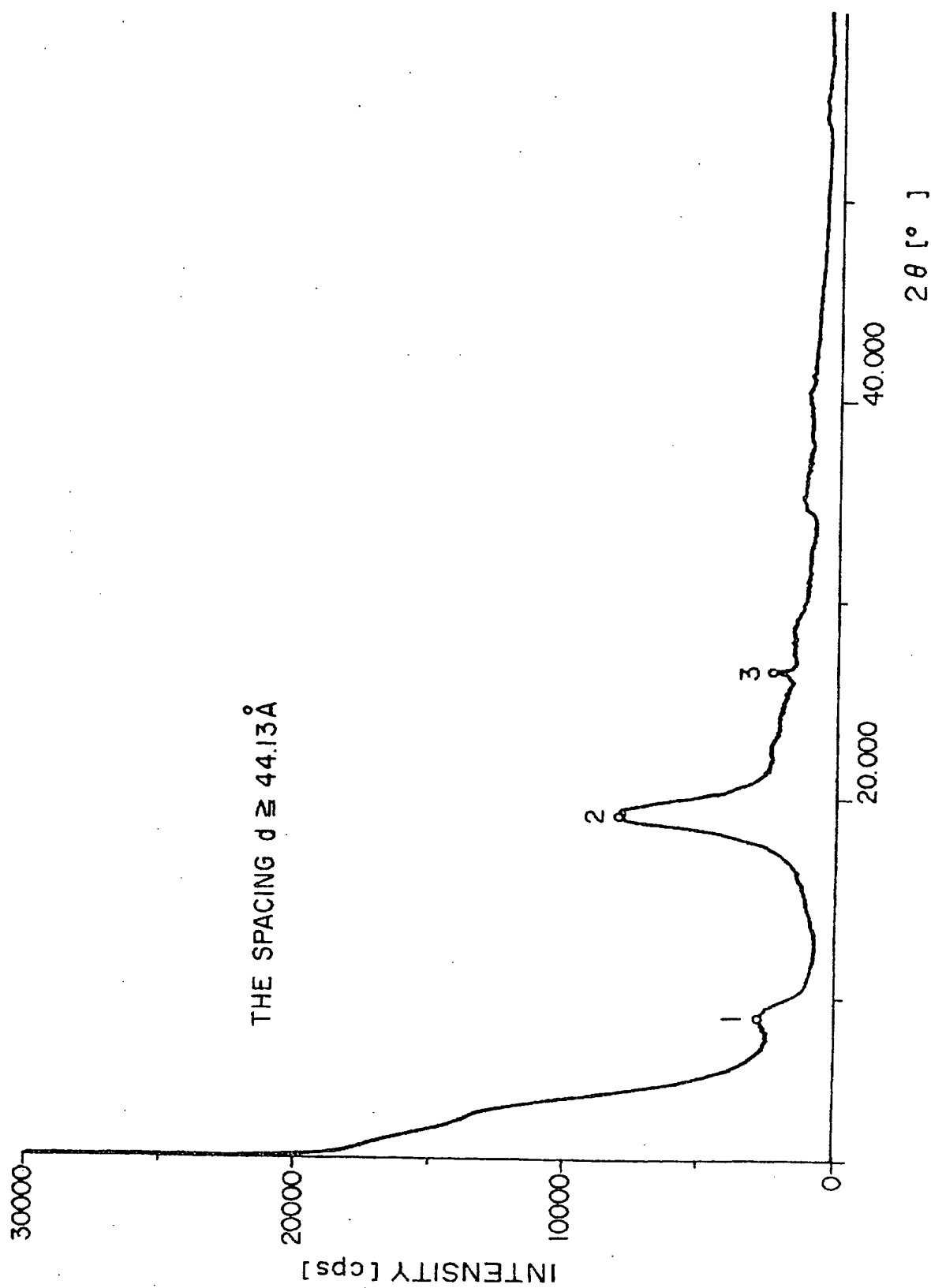
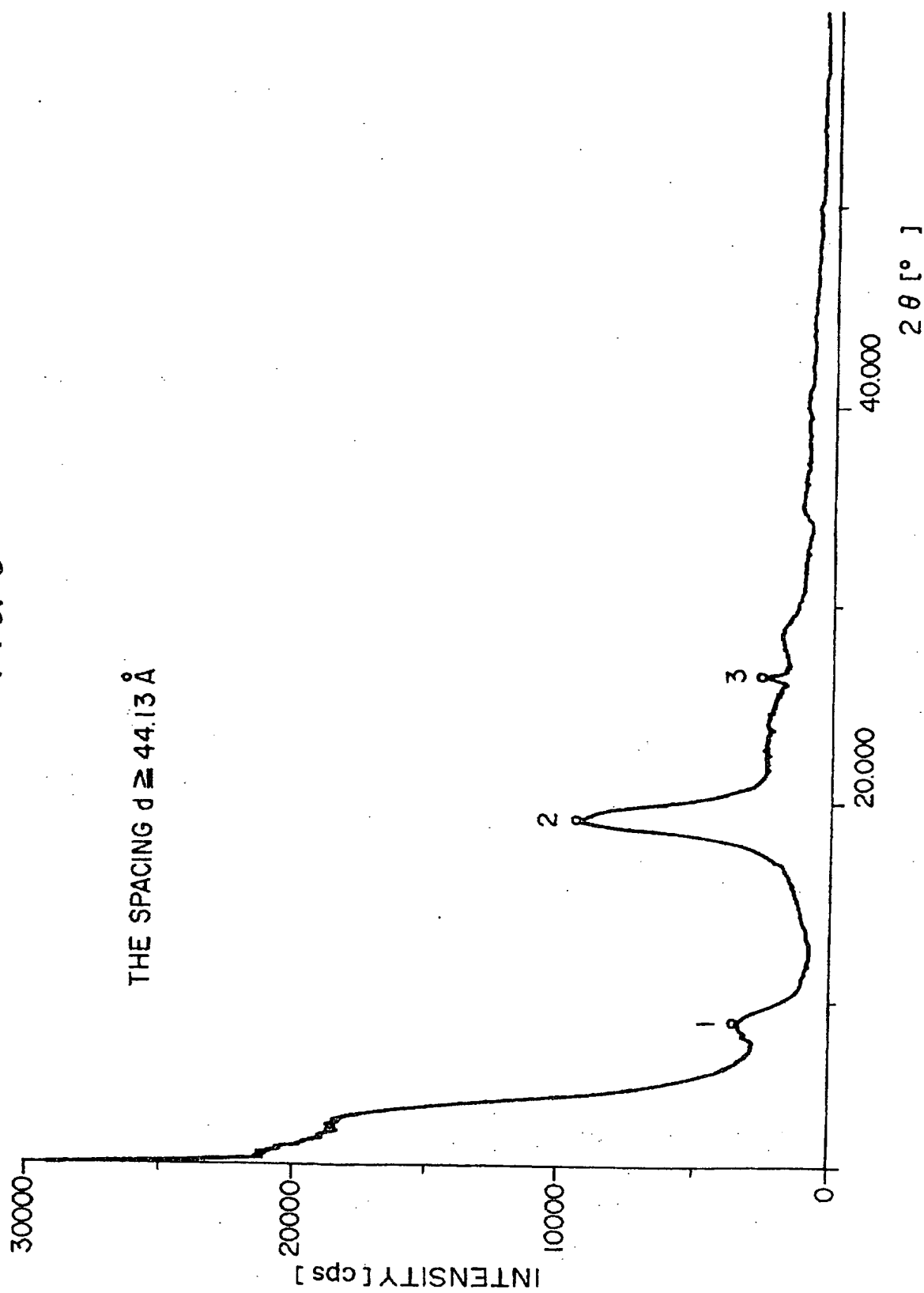


FIG. 9



GAS BARRIER RESIN COMPOSITION AND ITS FILM AND PROCESS FOR PRODUCING THE SAME

CROSS-REFERENCES TO RELATED APPLICATIONS

This is a continuation-in-part of application Ser. No. 08/384,798 filed Feb. 6, 1995, now abandoned, which is a continuation of application Ser. No. 08/097,889 filed Jul. 28, 1993, now abandoned, the complete disclosures of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a resin composition, film or laminate excellent in gas barrier properties and to a process for producing the same.

2. Description of the Related Art

Many functions are required for packaging, including adequate gas barrier properties for protecting the packaged contents. Gas barrier properties are important properties which affect the preservability of foods. Change in distributive systems, diversification of packaging techniques, additive regulations and change in taste increase more and more the necessity for adequate gas barrier properties. However, the gas barrier properties have been weak points of general plastics.

The food-deteriorating factors are oxygen, light, heat, water and the like, and in particular, oxygen is a serious factor. Gas barrier materials are indispensable for effectively intercepting oxygen and simultaneously for controlling the deterioration of foods such as gas-filling, vacuum packaging and the like. Since the barrier materials have a barrier function to not only oxygen gas but also other various gases, organic solvent vapors, fragrance and the like, they can be used for anticorrosion, deodorization and antisublimation and have been utilized in many fields of foods, cosmetics, agricultural chemicals, pharmaceuticals and the like in forms such as confectionery, bonito pack, retort pouch, mineral water container and the like.

Of films consisting of a thermoplastic resin, oriented films of polypropylene, polyester, polyamide or the like have excellent mechanical properties, heat resistance, transparency and the like and are widely used as packaging materials. However, when these films are used for packaging foods, they are unsatisfactory in barrier properties to oxygen and other gases, and therefore, they tend to cause such various problems insofar as their contents become deteriorated by oxidative degradation or with aerobic bacteria, fragrant components permeate the films to lose the taste of the contents, and the moisture in the atmosphere wets the contents to make the taste bad. Thus, usually, such a measure is often taken that other film layers having good gas barrier properties are laminated thereto.

Heretofore, various transparent plastic materials having unsatisfactory gas barrier properties have been known and there are, for example, films composed of polyvinyl alcohol, ethylene-vinyl alcohol copolymer or polyvinylidene dichloride resin. However, these plastic materials are oxygen-permeable in such a degree that the amount of oxygen permeated cannot be neglected while a metal or glass material to be used in canning or bottling has an oxygen permeability of substantially zero.

Another method for imparting gas barrier properties is a method of dispersing an inorganic material in the flat form

in a resin. For example, Japanese Patent Application Kokai No. 62-148,532 describes a production method which comprises coating on a releasable substrate a coating composition consisting of 100 parts by weight of a polyurethane resin solution having a concentration of 30% in 1,6-hexanepolycarbonate diol, 25 parts by weight of mica powder and 60 parts by weight of dimethyl-formamide, drying the same and then releasing it from the substrate.

Japanese Patent Application Kokai No. 64-043,554 describes a method of obtaining a film which comprises adding mica particles having an average length of 7 μ m and an aspect ratio of 140 to a methanolic aqueous solution of an ethylene-vinyl alcohol copolymer, pouring the solution in a cold water to form a precipitate, removing the precipitate by filtration, drying it to form pellets and then forming the pellets into a film.

Further, Japanese Patent Application Kokai No. 3-93,542 describes a method which comprises coating a biaxially oriented polyethylene terephthalate (OPET) film with a coating composition consisting of a silyl group-containing modified polyvinyl alcohol and synthetic hectorite at a weight ratio of 50:50, drying the same and then heat-treating it at 130°–150° C.

However, the films obtained by these techniques are still not sufficient in gas barrier properties and cannot always be said to be satisfactory.

SUMMARY OF THE INVENTION

In order to solve the above-mentioned problems, the present inventors have made extensive research to find that a resin composition consisting of a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound can be given excellent gas barrier properties by increasing the aspect ratio of the non-film-forming inorganic laminar compound.

An object of this invention is to provide a gas barrier resin composition or its molded article including a film having high level gas barrier and moisture barrier properties.

Another object of this invention is to provide a process for producing the gas barrier resin composition or its molded article including a film.

Other objects and advantages of this invention will become apparent from the following description.

According to this invention, there is provided a resin composition or its film or laminate comprising a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound having a particle size of 5 μ m or less and an aspect ratio of 50 to 5,000.

This invention further provides a process for producing the above resin composition or its film, which comprises dispersing a non-film-forming inorganic laminar compound in a high hydrogen-bonding resin or resin solution in the state that the non-film-forming inorganic laminar compound is swollen or cloven with a solvent, and removing the solvent from the dispersion, if necessary in the form of a film, while keeping said state.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph typically showing a relationship between X-ray diffraction peaks of an inorganic laminar compound and "the unit thickness a" of the inorganic laminar compound. In FIG. 1, 11 indicates the peak which corresponds to "the unit thickness a" of the inorganic laminar compound.

FIG. 2 is a graph typically showing a relationship between X-ray diffraction peaks of a resin composition containing an

inorganic laminar compound and "the spacing d " of the resin composition. In FIG. 2, 21 indicates the peak which corresponds to "the spacing d " of the resin composition, 22 indicates a position of the peak which corresponds to "the unit thickness a " of the inorganic laminar compound, 23 indicates the base line, k value, when it is converted into a length, and is not less than the width of one chain of the resin, and θ_d is a diffraction angle which corresponds to the sum of the unit thickness a and the width of one chain of the resin.

FIG. 3 is a graph typically showing a relationship between X-ray diffraction peaks of a resin composition and "the spacing d " of the resin composition when the detection of the peak which corresponds to the spacing d is disturbed by being overlapped with a halo (or background). In FIG. 3, the peak which corresponds to the spacing d is defined by the peak of the area from which the part below the base line at the angle range of lower than $2\theta_d$ is removed. 31 indicates the width of one chain of the resin, 32 indicates the base line, and 33 indicates the peak which corresponds to "the unit thickness a " of the inorganic laminar compound.

FIG. 4 is a graph showing X-ray diffraction peaks of the composition of polyvinyl alcohol, PVA-117H/Kunipia F used in Examples.

FIG. 5 is a graph showing X-ray diffraction peaks of Kunipia F used in Examples.

FIG. 6 is a graph showing x-ray diffraction peaks of the composition having the spacing d of 19.62 Å (which is a pattern in FIG. 2 as mentioned above).

FIG. 7 is a graph showing X-ray diffraction peaks of the composition having the spacing d of 32.94 Å (which is a pattern in FIG. 2 or FIG. 3 as mentioned above).

FIG. 8 is a graph showing X-ray diffraction peaks of the composition having the spacing d of 44.13 Å or more (which is a pattern in FIG. 3 as mentioned above).

FIG. 9 is a graph showing X-ray diffraction peaks of the composition having the spacing d of 44.13 Å or more (which is a pattern in FIG. 3 as mentioned above). However, in this case a clear shoulder, as compared with FIG. 8, due to the peak observed in lower angle range than the diffraction peak put a mark 1. is observed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The non-film-forming inorganic laminar compound used in this invention is an inorganic compound having a laminar structure formed by unit crystal layers being piled up on one another, and any inorganic compound may be used so long as it has a particle size of 5 μm or less and an aspect ratio of 50–5,000. In view of the gas barrier properties, the aspect ratio is preferably 200–3,000. If the aspect ratio is less than 50, the gas barrier properties are not sufficiently exhibited, and if the aspect ratio is more than 5,000, such an inorganic compound is technically difficult to produce and is too expensive.

The term "non-film-forming" used in the present invention means that the inorganic laminar compound exhibits insufficient gas barrier properties when subject to such process steps as blanching of a film, exfoliation of part of a film or formation of many piercing holes in a film at the time of film-forming.

In view of easy dispersion of the inorganic laminar compound in a resin, the non-film-forming inorganic laminar compound used in the present invention preferably has 500 cc- $\mu\text{m}^2/\text{day/atm}$ or more of a product of a coating film

thickness and oxygen-permeability measured for a film obtained by film-forming under the conditions shown in Comparative Examples 27–29.

When the particle size is 3 μm or less, the transparency is higher and such an inorganic compound is preferred.

Specific examples of the non-film-forming inorganic laminar compound include graphite, phosphoric acid salt derivative type compounds (e.g. zirconium phosphate compounds), chalcogenides [the IV Group metal (Ti, Zr, Hf) dichalcogenides, the V Group metal (V, Nb, Ta) dichalcogenides and the VI Group metal (Mo, W) dichalcogenides which are represented by the formula MX_2 , wherein X represents chalcogen (S, Se, Te)], clay minerals and the like.

The measurement of true particle size in a resin composition is very difficult, and therefore, the particle size of the non-film-forming inorganic laminar compound used in this invention is a value determined according to a dynamic light-scattering method in a solvent.

When a non-film-forming inorganic laminar compound sufficiently swollen with the same solvent as used in the dynamic light-scattering method is compounded with a resin, the particle size of the non-film-forming inorganic laminar compound in the resin can be considered to be close to the particle size in a solvent.

The aspect ratio (Z) of the non-film-forming inorganic laminar compound used in this invention is indicated by the relation of $Z=L/a$ in which L is the particle size determined according to the dynamic light-scattering method in a solvent and a is the unit thickness of the non-film-forming inorganic laminar compound (the unit thickness a is a value determined by measurement of the non-film-forming inorganic laminar compound alone according to the powder X-ray diffraction), provided that in $Z=L/a$, the spacing d determined by the powder X-ray diffraction of the composition is present and satisfies a relation of $a < d$, in which the value of $d-a$ is required to be greater than the width of one chain of resin in the composition.

Specifically, the unit thickness a is defined by the spacing determined from an angle θ which corresponds to the peak at the lowest angle among the observed diffraction peaks, on a basis of the Bragg's Equation ($n\lambda=2D\sin\theta$, $n=1, 2, 3, \dots$) as typically shown in FIG. 1 having 2θ as a horizontal axis and an intensity of X-ray diffraction peak as a vertical axis (the details of the powder X-ray diffraction method can be referred to, for example, "Manual for Instrumental Analysis (a)", Edited by Jiro Shiokawa and Published by Kagaku Dojin, Japan, page 69, 1985).

As typically shown in FIG. 2 having 2θ as a horizontal axis and an intensity of X-ray diffraction peak as a vertical axis, the spacing d ($a < d$) is a spacing which corresponds to the peak at the lowest angle among the diffraction peaks observed in lower angle (large spacing) range than the diffraction peak which corresponds to the unit thickness a as mentioned above. As typically shown in FIG. 3, when the detection of the peak which corresponds to the spacing d as mentioned above is disturbed by being overlapped with a halo (or background), the peak which corresponds to the spacing d is defined by the peak of the area from which the part below the base line at the angle range of lower than $2\theta_d$ is removed. " θ_d " is herein a diffraction angle which corresponds to the sum of the unit thickness a and the width of one chain of the resin (the details of the method for determining the spacing d can be referred to, for example, "Encyclopedia of Clay", Edited by Shuichi Iwao et al., Published by Asakura Shoten, Japan, page 35 et seq. and page 271 et seq., 1985).

In this way, "integrated intensity" of the diffraction peak (which corresponds to the spacing d) observed in the powder X-ray diffraction of the resin composition is preferably 2 or more (more preferably, 10 or more) of a relative ratio to the integrated intensity of the base diffraction peak (which corresponds to the unit thickness a).

Z cannot necessarily be said to be the true aspect ratio of the non-film-forming inorganic laminar compound in the resin composition; however, it is considerably reasonable for the following reason:

The aspect ratio of the non-film-forming inorganic laminar compound in the resin composition is very difficult to measure directly. Between the spacing d obtained by the powder X-ray diffraction of the composition and the unit thickness a determined by the powder X-ray diffraction of the non-film-forming inorganic laminar compound, there is a relation of $a < d$, and when the d - a value is greater than the width of one chain of the resin in the composition, it follows that in the resin composition, the resin is inserted between the layers of the non-film-forming inorganic laminar compound, and hence, it is clear that the thickness of the non-film-forming inorganic laminar compound is the unit thickness a .

"The width of one chain of the resin" can be determined by a simulation calculation etc. (for example, referred to "Introduction of Polymer Science", Published by Kagaku Dojin, Japan, pages 103-110, 1981). That of poly(vinyl alcohol) was determined to be 4 to 5 Å (that of water molecule was determined to be 2 to 3 Å).

Also, the measurement of the true particle size in the resin composition is very difficult, and taking the case where the non-film-forming inorganic laminar compound is sufficiently swollen with the same solvent as used in the dynamic light-scattering method and then compounded with the resin, it can be understood that the particle size of the non-film-forming inorganic laminar compound in the resin is considerably close to that in the solvent, provided that the particle size L determined by the dynamic light-scattering method is considered not to exceed the long diameter L_{max} , so that the true aspect ratio L_{max}/a cannot theoretically become lower than Z in the definition of the aspect ratio in this invention.

From the above two points, it is considered that the aspect ratio in this invention be relatively high in propriety. In this invention, the aspect ratio and particle size mean the above-defined aspect ratio and particle size, respectively.

The non-film-forming inorganic laminar compound having a large aspect ratio is preferably an inorganic laminar compound which can be swollen or cloven with a solvent.

The degree of "swelling and cleavage" properties to a solvent of the inorganic laminar compound used in the present invention can be determined by the following "swelling and cleavage" tests. The swelling property of the inorganic laminar compound is preferably 5 or more (more preferably, 20 or more). This cleavage property of the inorganic laminar compound is preferably 5 or more (more preferably, 20 or more). In these cases, a solvent having a smaller density than that of the inorganic laminar compound is used as a solvent. When the inorganic laminar compound is natural swellable clay minerals, water is preferably used as the solvent.

[Swelling Test]

2 g of an inorganic laminar compound was slowly added to 100 ml of a solvent (100 ml of a measuring cylinder was used as a container). After leaving to stand at 23° C. for 24 hours, a volume of a dispersed layer of the inorganic laminar compound was measured from the scale of a boundary

between the dispersed layer of the inorganic laminar compound and a supernatant liquid. The larger the value of the volume, the higher the swelling property (swellability). [Cleavage Test]

30 g of an inorganic laminar compound was slowly added to 1500 ml of a solvent and dispersed in the solvent at a peripheral speed of 8.5 m/sec at 23° C. for 90 minutes by the use of a dispersing machine (manufactured by Asada Tekko, trade name: Desper MH-L, a diameter of an impeller blade: 52 mm, a number of agitating: 3100 rpm, a container volume: 3l, a distance between the bottom of the container and the impeller blade: 28 mm). Thereafter, 100 ml of the dispersed solution was taken and added to a measuring cylinder, left to stand for 60 minutes, and then the volume of the dispersed layer of the inorganic laminar compound was measured from the scale of the boundary between the dispersed layer of the inorganic laminar compound and a supernatant liquid.

Among the inorganic laminar compounds which can be swollen or cloven with a solvent, non-film-forming clay minerals having a swellability are more preferable. The clay minerals are classified into a type of a two-layer structure in which on the upper portion of the tetrahedron layer of silica is present an octahedron layer in which the center metal is aluminum, magnesium or the like, and a type of a three-layer structure in which an octahedron layer in which the center metal is aluminum, magnesium or the like is sandwiched between tetrahedron layers of silica.

The former type includes the kaolinite Group, the antigorite Group and the like. The latter type includes the smectite Group, the vermiculite Group, the mica Group and the like corresponding to the number of cations between the layers.

Specifically, kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, sodium terasilic mica, sodium taeniolite, common mica, margarite, talc, vermiculite, phlogopite, xanthophyllite, chlorite and the like.

The solvent for swelling the non-film-forming inorganic laminar compound is not critical; however, in the case of, for example, natural swellable non-film-forming clay minerals, preferable are water; alcohols such as methanol, ethanol, propanol, isopropanol, ethylene glycol, diethylene glycol and the like; dimethylformamide; dimethylsulfoxide; acetone; and the like. Water and alcohols such as methanol and the like are more preferable.

The high hydrogen-bonding resin used in this invention is not critical and includes, for example, polyvinyl alcohol (PVA), ethylene-vinyl alcohol copolymer (EVOH), polysaccharide, polyacrylic acid and its esters, and the like. It is preferred that the high hydrogen-bonding resins satisfy the requirement that the weight percentage of hydrogen-bonding group or ionic group per unit weight of the resin falls within the range of 20-60%.

It is more preferred that the high hydrogen-bonding resins satisfy the requirement that the weight percentage of the hydrogen-bonding group or ionic group per unit weight of the resin falls within the range of 30-50%. The hydrogen-bonding group of the high hydrogen-bonding resin includes hydroxyl group, amino group, thiol group, carboxyl group, sulfonic acid group, phosphoric acid group and the like, and the ionic group includes carboxylate group, sulfonate ion group, phosphate ion group, ammonium group, sulfonium group and the like.

Of the hydrogen-bonding groups or ionic groups of the high hydrogen-bonding resins, more preferable are hydroxyl group, amino group, carboxyl group, sulfonic acid group, carboxylate group, sulfonate ion group, ammonium group and the like.

Specific examples of the high hydrogen-bonding resin include, for example, polyvinyl alcohol, ethylene-vinyl alcohol copolymer, the vinyl alcohol fraction of which is 41 mole % or more, polysaccharide such as hydroxymethylcellulose, hydroxyethylcellulose, carboxymethylcellulose, amylose, amylopectin, pluran, cardran, xanthan, chitin, chitosan, cellulose and the like; polyacrylic acid; polysodium acrylate; polybenzenesulfonic acid; polysodium benzenesulfonate, polyethyleneimine; polyallylamine; its ammonium salt; polyvinyl thiol; polyglycerin; and the like.

More preferable high hydrogen-bonding resins are soluble resins in solvents which can swell and cleave the inorganic laminar compound, such as polyvinyl alcohol and polysaccharide etc.

The term "polyvinyl alcohol" referred to herein means a polymer having a monomer unit of vinyl alcohol as a main component. Such a "polyvinyl alcohol" includes, for example, a polymer obtained by hydrolyzing or ester interchanging (saponifying) the acetate ester portion of a vinyl acetate polymer (exactly, a polymer in which a copolymer of vinyl alcohol and vinyl acetate is formed), and polymers obtained by saponifying a trifluorovinylacetate polymer, a vinyl formate polymer, a vinyl pivalate polymer, a tert-butylvinylether polymer, a trimethylsilylvinylether polymer, and the like (the details of "polyvinyl alcohol" can be referred to, for example, "World of PVA", Edited by the Poval Society and Published by Kobunshi Kankoukai, Japan, 1992 and "Poval", Edited by Nagano et al. and Published by Kobunshi Kankoukai, Japan, 1981). The degree of saponification in polyvinyl alcohol is preferably 70 mole % or more, more preferably 85 mole % or more, particularly preferably 98 mole % or more, that is, so-called perfect saponification. The degree of polymerization of polyvinyl alcohol is preferably 100 to 5,000, more preferably 200 to 3,000.

The term "polysaccharide" used herein means biopolymers which are synthesized by condensation-polymerization of various monosaccharides in a living body, and includes chemically modified biopolymers. The polysaccharides include, for example, cellulose; cellulose derivatives such as hydroxymethylcellulose, hydroxyethylcellulose, carboxymethylcellulose and the like; amylose; amylopectin; pluran; cardran; xanthan; chitin; chitosan and the like.

In this invention, a cross-linking agent for the hydrogen-bonding group may be used for the purpose of improving the barrier properties of the resin after water-resistant environmental test.

The cross-linking agent for hydrogen-bonding group is not critical, and includes, for example, titanium coupling agent, silane coupling agent, melamine coupling agent, epoxy coupling agent, isocyanate coupling agent, copper compound, zirconium-containing compound and the like, and preferable is the zirconium-containing compound.

Specific examples of the zirconium-containing compound include, for example, zirconium halides such as zirconium oxychloride, zirconium hydroxychloride, zirconium tetrachloride, zirconium bromide and the like; zirconium salts with mineral acids such as zirconium sulfate, basic zirconium sulfate, zirconium nitrate and the like; zirconium salts with organic acids such as zirconium formate, zirconium acetate, zirconium propionate, zirconium caprylate, zirconium stearate and the like; zirconium complexes such as ammonium zirconium carbonate, sodium zirconium sulfate, ammonium zirconium acetate, sodium zirconium oxalate, sodium zirconium citrate, ammonium zirconium citrate and the like; etc.

The amount of the cross-linking agent for hydrogen-bonding group added is not particularly limited so long as the ratio (K) of the number of moles (CN) of the cross-linking group of the cross-linking agent to the number of moles (HN) of the hydrogen-bonding group of the high hydrogen-bonding resin (namely, $K=CN/HN$) falls within the range of 0.001 to 10, and preferably within the range of 0.01 to 1.

The composition ratio (volume ratio) of the non-film-forming inorganic laminar compound to the high hydrogen-bonding resin used in this invention is generally in the range of 5/95-90/10, preferably in the range of 5/95-50/50.

When the volume ratio of the non-film-forming inorganic laminar compound is less than 5/95, the barrier properties are not sufficient, and when it is more than 90/10, the film-formability is not satisfactory.

The volume ratio can be calculated from the weight ratio of the inorganic laminar compound charged to the resin charged expressed by a fraction. Specifically, it can be calculated by dividing the numerator and the denominator of the fraction by the densities of the inorganic laminar compound charged and the resin charged, respectively. Generally, the density of a resin (for example, polyvinyl alcohol) sometimes varies with crystallinity of the resin, however, in the calculation of the volume ratio as mentioned above, it can be calculated, for example, on the assumption that crystallinity of polyvinyl alcohol is 50%.

The method of compounding the non-film-forming inorganic laminar compound with the high hydrogen-bonding resin is not critical, and includes, for example, a method which comprises mixing a resin solution with a dispersion formed by previously swelling or cleaving the non-film-forming inorganic laminar compound with a solvent and then removing the solvent; a method which comprises adding a dispersion formed by swelling or cleaving the non-film-forming inorganic laminar compound with a solvent to the resin, and then removing the solvent; a method which comprises adding non-film-forming inorganic laminar compound to a solution, dissolving a high hydrogen-bonding resin to form a dispersing solution containing a swollen and cloven non-film-forming inorganic laminar compound and removing a solvent from the solution; and a method which comprises heat-mixing the high hydrogen-bonding resin with the non-film-forming inorganic laminar compound. The former three are preferable since a particularly large aspect ratio is easily obtained.

In the above-mentioned former three methods, heat-aging at a temperature of 110° C. to 220° C. after the removal of the solvent can enhance the water resistance of a film (the barrier properties after water-resistant environmental test). The ageing time is not critical, and it is necessary that the film temperature reaches at least the desired temperature. For example, in the case of contacting with a heating medium such as using a hot air drier, a period of 1 second to 100 minutes is preferred.

The heat source is not critical, and contact with hot roll, contact with a heating medium such as hot air or oil, heating with an infrared ray, heating with a microwave and other various means can be applied.

The effect of the water resistance referred to herein is remarkably high when the non-film-forming inorganic laminar compound is a non-film-forming clay mineral.

The resin composition of this invention is molded into various forms and then used. The form of the molded article is not critical, and when the molded article is used as a packaging material such as film, sheet, container (e.g. tray, bottle or the like), etc., gas barrier properties are sufficiently exhibited.

The molded article is usually used in the form of a laminate. The substrate of the laminate is not critical, and general substrates such as resin, paper, aluminum foil, wood, woven fabric, non-woven fabric and the like may be used.

The resin to be used as a substrate includes polyolefin resins such as polyethylene (low density and high density), ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-hexene copolymer, ethylene-octene copolymer, polypropylene, ethylene-vinyl acetate copolymer, ethylene-methyl methacrylate copolymer, ionomer resin and the like; polyester resins such as polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate and the like; polyamide resins such as nylon-6, nylon-6.6, meta-xylenediamine-adipic acid condensation polymer, polymethyl methacrylimide and the like; acrylic resins such as polymethyl methacrylate and the like; styrene or acrylonitrile resins such as polystyrene, styrene-acrylonitrile copolymer, styrene-acrylonitrile-butadiene copolymer, polyacrylonitrile and the like; hydrophobized cellulose resins such as cellulose triacetate, cellulose diacetate and the like; halogen-containing resins such as polyvinyl chloride, polyvinylidene dichloride, polyvinylidene difluoride, Teflon and the like; hydrogen-bonding resins such as polyvinyl alcohol, ethylene-vinyl alcohol copolymer, cellulose derivatives and the like; engineering plastic resins such as polycarbonate resin, polysulfone resin, polyethersulfone resin, polyetheretherketone resin and the like; etc.

In the case of laminates in the form of a film, the outer layer is preferably a biaxially oriented polypropylene, polyethylene terephthalate or nylon film, a polyvinylidene dichloride-coated (so-called K-coat) biaxially oriented polypropylene, polyethylene terephthalate or nylon film or the like, and the inner layer is preferably a polyolefin resin film such as polyethylene (low density or high density) film, ethylene-propylene copolymer film, ethylene-butene copolymer film, ethylene-hexene copolymer film, ethylene-octene copolymer film, polypropylene film, ethylene-vinyl acetate copolymer film, ethylene-methyl methacrylate copolymer film or the like in view of good heat-sealability.

The method of laminating the resin composition of this invention to a substrate is not critical. When the substrate is a film or sheet, preferred is a coating method which comprises coating a coating solution of the resin composition on the surface of the substrate, drying the solution and then heat-treating the coated substrate or a method which comprises laminating the film of this invention to a substrate.

The coating method includes direct gravure method; reverse gravure method; microgravure method; roll-coating methods such as two-roll beat coat method, bottom-feeding three-roll reverse coat method and the like; doctor knife method; die coat method; dip coat method; bar coating method and combinations thereof.

The coating layer thickness may be varied depending upon the kind of substrate and the desired barrier properties, and it is preferably 10 μm or less, more preferably 1 μm or less, in terms of dry thickness.

When it is 1 μm or less, the transparency of the laminate is greatly high. The resin composition, laminate, and laminated film of the present invention preferably have a transparency selected in view of a convenience. The transparency is preferably 80% or more of the total light transmission at a wavelength of 500 nm, more preferably 85% or more, particularly preferably 90% or more. Such a transparency can be suitably measured by, for example, a commercially available spectrophotometer (self-spectrophotometer, type 330, manufactured by Hitachi, Ltd.).

There is no lower limit, and the thickness is preferably 1 nm or more, more preferably 10 nm or more, particularly

preferably 100 nm or more, in order to obtain effective gas barrier properties.

As far as the effect of this invention is not lost, the resin composition of this invention may contain various additives such as ultraviolet absorber, coloring matter, antioxidant and the like. This invention covers a laminated film and laminate which have at least one layer of the above-mentioned film.

According to this invention, it becomes possible to obtain a gas barrier film having high levels of gas barrier and moisture barrier properties not obtainable from conventional films. This is achieved by using a non-film-forming inorganic laminar compound having a particle size of 5 μm or less and an aspect ratio of 50-5,000 in a mixture of a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound.

As stated in Examples which appear hereinafter, when the non-film-forming inorganic laminar compound is not contained, the barrier properties are greatly inferior to this invention even if the same resin is used (see, for example, Example 1 and Comparative Example 1). Even if the resin composition is composed of a high hydrogen-bonding resin and an inorganic laminar compound, when the inorganic laminar compound has an aspect ratio of about 30, the barrier properties are inferior 100 times or more to the Examples of this invention (see, for example, Comparative Example 3 and Example 1). In the Examples, the barrier properties are greatly different between the case of an aspect ratio of about 100 and the case of an aspect of about 500, and the barrier-imparting effect is greatly changed at an aspect ratio of about 200. When the aspect ratio is more than 200, a greater barrier-enhancing effect can be expected.

In the process for forming a film by adding to a resin or a resin solution a dispersion formed by swelling or cleaving a non-film-forming inorganic laminar compound with a solvent and removing the solvent, heat-aging after the removal of the solvent (for example, at 150° C. for 10 minutes) greatly enhances the barrier properties of the film after water-resistant environmental test as compared with the case in which no heat-aging is effected. This means that when the film is used in packaging foods, the package is resistant to high temperature and moisture conditions, boiling treatment or retort treatment, and the film is very much useful in practice.

Moreover, the addition of a cross-linking agent for the hydrogen-bonding group (ammonium zirconium carbonate is used in this case) greatly enhances the barrier properties of the film after water-resistant environmental test. When this is combined with the above-mentioned heat-aging treatment, the effect is further increased, and the resulting film is more preferably used in packaging foods which may be subjected to high temperature and moisture conditions, boiling treatment or retort treatment.

The resin composition of this invention has so high level barrier properties as not to be predicted from conventional resin materials. The oxygen-permeability per μm of thickness of the film of this invention is not more than 2 cc/m²/day/atm, or in some cases not more than 0.2 cc/m²/day/atm, under the conditions that the temperature is 31° C. and the relative humidity is 61%, while even the ethylene-vinyl alcohol copolymer which has the best oxygen barrier properties among commercially available resins has an oxygen-permeability of 15 cc/m²/day/atm. Further, the ethylene-vinylalcohol copolymer remarkably deteriorates in its gas barrier property at high humidity exceeding 90% RH. As shown in Comparative Examples 25 and 26, its oxygen-permeability per μm exceeds 90 cc/m²/day/atm at a condition of 23.8° C., 94.5% RH. On the other hand, according to

Examples 34-45, especially Example 45 of the present invention, oxygen-permeability per μm under the same condition as above is $0.06 \text{ cc/m}^2/\text{day/atm}$. This fact indicates that a film of the present invention has a very superior gas barrier property even at high humidity. The resin composition of this invention is greatly superior in barrier properties to conventional resins and is close to metal and ceramic in respect of barrier properties. Therefore, the resin composition can be used in uses requiring a metal such as aluminum foil or an inorganic material such as glass in view of the gas barrier properties of the composition. Thus, the resin composition of this invention can be said to be a material which has broken down the common knowledge of gas barrier resin composition (such weak points of metal and ceramic that the former is opaque and the latter is brittle can be overcome by the resin composition of this invention).

That is to say, the resin composition of this invention can be used in the form of a film in packaging miso, sliced dried bonito, confectionery, noodle, ham, sausage, boiled rice, curry, stew and the like; in the form of a bottle as a squeeze bottle for mayonnaise or a container for juice, soy source, edible oil and the like; and can further be used for packaging industrial materials in medical, electronic, chemical and mechanical fields such as blood transfusion pack, semiconductor package, oxidative chemicals package, precision parts package and the like. Thus, the resin composition of this invention can be used in various forms in a wide field.

This invention is explained in more detail below referring to Examples; however, this invention is not limited to these Examples.

Various physical properties were measured by the following methods.

[Oxygen-permeability]

Measured by an oxygen-permeability measuring apparatus (OX-TRAN 10/50A manufactured by MOCON) at a temperature of 31°C . (moisture-controlling constant temperature bath: 21°C .) (the relative humidity was 61%).

[Thickness]

Measured by means of a digital thickness meter when the thickness is $0.5 \mu\text{m}$ or more or by means of a gravimetric analysis (the measured weight of a film having a unit area is divided by the area and then divided by the specific density of the composition) when the thickness is less than $0.5 \mu\text{m}$, or by an elemental analysis in the case of a laminate of the resin composition of this invention to a substrate (the ratio of the thickness of the resin composition layer to the thickness of the substrate is determined from the ratio of the analysis value of the specific inorganic element (resulting from the composition layer) of the laminate to the analysis value of the specific element of inorganic laminar compound alone).

[Particle size]

Measured by an ultrafine particle size analyzer (BI-90 manufactured by Brookhaven) at a temperature of 25°C . in an aqueous solvent. The center diameter determined from the photon correlation method according to a dynamic light-scattering method is taken as particle size L.

[Aspect ratio calculation]

Using an X-ray diffractometry (XD-5A manufactured by Shimadzu Seisakusho), the inorganic laminar compound alone and the resin composition were subjected to diffraction measurement by a powder method to determine the spacing (a unit thickness) of the inorganic laminar compound, and it was confirmed from the diffraction measurement of the resin composition that there was a portion in which the spacing of the inorganic laminar compound was broadened. Using the

particle size L determined by the above-mentioned method, the aspect ratio Z was determined from the equation $Z=L/a$.

EXAMPLE 1

Synthetic mica [terasillic mica (Na-Ts) manufactured by Topy Kogyo] was dispersed in ion-exchanged water ($0.7 \mu\text{S/cm}$ or less) in a proportion of 0.65% by weight. This dispersion is used hereinafter as a non-film-forming inorganic laminar compound dispersion (Liquid A). The particle size of the synthetic mica (Na-Ts) was 977 nm , and the value obtained from the powder X-ray diffraction was 0.9557 nm , and the aspect ratio Z was 1043. Polyvinyl alcohol (PVA 210 manufactured by Kuraray, saponification degree: 88.5%, polymerization degree: 1,000) was dissolved in deionized water ($0.7 \mu\text{S/cm}$ or less) in a concentration of 0.325% by weight. The resulting solution is used hereinafter as a high hydrogen-bonding resin solution (Liquid B). Liquid A and Liquid B were mixed so that the solid component ratio (volume ratio) [non-film-forming inorganic laminar compound/high hydrogen-bonding resin] was 3/7. The resulting mixture is used hereinafter as a coating solution. The coating solution was applied onto a substrate obtained by subjecting a triacetylcellulose (TAC) film (FUJITAC CLEAR manufactured by Fuji Photo Film Co., Ltd.) having a thickness of $76 \mu\text{m}$ to surface saponification treatment, and then dried at room temperature to obtain a gas barrier film. The dry thickness of the coating layer was $0.87 \mu\text{m}$. The oxygen-permeability of the resulting laminated film at 31°C . and 61% RH was $0.092 \text{ cc/m}^2/\text{day}$. This value was reduced to that in the case where the dry coating thickness was $1.0 \mu\text{m}$ to obtain an oxygen-permeability at 31°C . and 61% RH of $0.08 \text{ cc/m}^2/\text{day}$. Hence, the laminated film was excellent in gas barrier properties.

EXAMPLE 2

The same procedure as in Example 1 was repeated, except that the high hydrogen-bonding resin of Liquid B was replaced with hydroxyethylcellulose (manufactured by Wako Junyaku Kogyo) to obtain a gas barrier film, which was then subjected to oxygen-permeability test. The result obtained is indicated in Table 1 which shows excellent gas barrier properties.

EXAMPLE 3

The same procedure as in Example 1 was repeated, except that the coating and drying were conducted using a direct gravure coater (Multicoater M-200 manufactured by Hirano Tech-Seed) by a direct gravure coating method (coating speed: 1.7 m/min , drying temperature: 80°C ., repeatedly coated 4 times) to obtain a gas barrier film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates excellent gas barrier properties.

EXAMPLE 4

The same procedure as in Example 1 was repeated, except that a direct gravure coater (Multicoater M-200 manufactured by Hirano Tech-Seed) by a direct gravure coating method (coating speed: 1.7 m/minute , drying temperature: 80°C ., repeatedly coated 4 times) and the substrate was replaced with a biaxially oriented polystyrene (OPS) film having a thickness of $25 \mu\text{m}$ [TYPE (TH) CO, corona-treated, manufactured by Asahi Chemical Industry Co., Ltd.] to obtain a gas barrier film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates excellent gas barrier properties.

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COMPARATIVE EXAMPLE 1

The same procedure as in Example 1 was repeated, except that Liquid A was not used and a 1% by weight solution of polyvinyl alcohol (PVA 210 manufactured by Kurarey, saponification degree: 88.55%, polymerization degree: 1,000) in deionized water (0.7 μ S/cm or less) was substituted for the Liquid B, to obtain a film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates inferior gas barrier properties.

COMPARATIVE EXAMPLE 2

The same procedure as in Example 1 was repeated, except that Liquid A was not used and a 2% by weight solution of hydroxyethylcellulose (HEC manufactured by Wako Junyaku Kogyo) in deionized water (0.7 μ S/cm or less) was substituted for the Liquid B, to obtain a film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates inferior gas barrier properties.

COMPARATIVE EXAMPLE 3

The same procedure as in Example 1 was repeated, except that the Liquid A was replaced with a dispersion obtained by dispersing synthetic hectorite [Laponite XLG manufactured by Nihon Silica Kogyo, particle size: 35 nm, a value: about 1 nm (diffraction peak was broad), aspect ratio: about 35] in deionized water (0.7 μ S/cm or less) in a proportion of 2% by weight and the Liquid B was replaced with a 1% by weight solution of polyvinyl alcohol (PVA 210 manufactured by Kurarey, saponification degree: 88.5%, polymerization degree: 1,000) in deionized water (0.7 μ S/cm or less), to obtain a film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates inferior gas barrier properties.

COMPARATIVE EXAMPLE 4

The same procedure as in Example 1 was repeated, except that Liquid B was not used, to prepare a film. However, the synthetic mica was peeled off from the laminated film and flaws showed horribly on the film surface, and the film-formability was inferior.

COMPARATIVE EXAMPLE 5

Triacetylcellulose (TAC) film (thickens: 76 μ m, FUJITAC CLEAR manufactured by Fuji Photo Film Co., Ltd.) had an oxygen-permeability at 61% RH as shown in Table 1 which indicates greatly inferior gas barrier properties.

COMPARATIVE EXAMPLE 6

A biaxially oriented polystyrene (OPS) film having a thickness of 25 μ m [TYPE (TH) CO, corona-treated, manufactured by Asahi Chemical Industry Co., Ltd.] had an oxygen-permeability at 31° C. and 61% RH as shown in Table 1 which indicates greatly inferior gas barrier properties.

EXAMPLE 5-15

The oxygen-permeabilities of films each composed of the non-film-forming inorganic laminar compound, high hydrogen-bonding resin and substrate shown in Table 2 in the proportions shown in Table 2 were measured. Each of the films was formed by coating on the substrate a coating solution consisting of Liquid A and Liquid B prepared in the same manner as in Example 1, except that both Liquids A and B had a concentration of 2% by weight, by a gravure coater (Testcoater NCR 3-230, CAG 150, CR3 manufac-

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tured by Yasui Seiki) by a microgravure coating method [coating speed: 1-3 m/minute, drying temperature: 60° C. (inlet heater) and 100° C. (outlet heater)].

The results obtained are shown in Table 2 which indicates excellent gas barrier properties.

COMPARATIVE EXAMPLES 7-13

The oxygen-permeabilities of films each composed of the inorganic laminar compound, resin and substrate shown in Table 2 in the proportions shown in Table 2 prepared in the same manner as in Examples 1-15 and the oxygen-permeability of the substrate alone were measured. The results obtained are shown in Table 2 which indicates inferior gas barrier properties.

EXAMPLES 16-25

Films each composed of the non-film-forming inorganic laminar compound, high hydrogen-bonding resin and substrate shown in Table 3 in the proportions shown in Table 3 which had been subjected to heat treatment after film-formation under the conditions shown in Table 3 were subjected to oxygen-permeability test before and after immersion in hot water. The films were prepared by coating the substrate with a coating solution prepared in the same manner as in Example 1, except that the concentrations of Liquids A and B were 2% by weight and a cross-linking agent for hydrogen-bonding group was added after the preparation of the coating solution consisting of Liquids A and B, by means of a gravure coater (Testcoater NCR 3-230, CAG 150, CR3 manufactured by Yasui Seiki) by a microgravure coating method [coating speed: 1-3 m/minute, drying temperature: 60° C. (inlet heater) and 100° C. (outlet heater)]. The heat treatment after film-formation was conducted by subjecting the films to treatment by a hot air dryer (Perfect Oven manufactured by Tabai Esupekku) at the predetermined temperature for the predetermined time. The oxygen-permeability test after immersion in hot water was conducted as follows: The sample was immersed in water at 60° C. for 13 hours, air dried, dried at 60° C. for 1 hour and then subjected to oxygen-permeability test.

The results obtained are shown in Table 3 which indicates excellent gas barrier properties. The films which had been heat-treated or films in which a cross-linking agent for the hydrogen-bonding group was used indicate remarkable enhancement of water resistance.

COMPARATIVE EXAMPLES 14-15

The oxygen-permeability test after immersion in hot water was conducted of films each composed of the inorganic laminar compound, resin, substrate and cross-linking agent shown in Table 3 in the proportions shown in Table 3, the films having been prepared by the same manner as in Examples 16-25 and heat-treated under the conditions shown in Table 3. The results obtained are shown in Table 3, which indicates inferior gas barrier properties and inferior water resistance.

EXAMPLES 26-33

Films each composed of the inorganic laminar compound, resin and cross-linking agent shown in Table 4 in the proportions shown in Table 4 which had been subjected to heat treatment after film-formation under the conditions shown in Table 4 were subjected to dissolution resistance test. The films were prepared by casting a coating solution prepared in the same manner as in Example 1, except that the concentrations of Liquids A and B were 2% by weight and the cross-linking agent was added after the preparation of the coating solution consisting of Liquids A and B, on an

acrylic resin plate so that the film thickness after drying became about 20 μm , and drying the resulting films at room temperature. The dissolution resistance test was conducted as follows: The film sample obtained was subjected to heat-treatment by a hot air dryer (Perfect Oven manufactured by Tabai Esupekkū) at the predetermined temperature for the predetermined time, wrapped with a stainless steel net, immersed in hot water at 80° C. for 10 minutes, taken out together with the stainless steel net, air-dried and then air-dried at 60° C. for 1 hour, after which the weight percentage of the remainder was determined (the higher the percentage of remainder, the better the water resistance). The results obtained are shown in Table 4 which indicates excellent water resistance.

COMPARATIVE EXAMPLES 16-24

Dissolution resistance test was conducted of films each composed of the inorganic laminar compound, resin and cross-linking agent shown in Table 4 in the proportions shown in Table 4 prepared in the same manner as in Examples 26-33. The results obtained are shown in Table 4 which indicates inferior water resistance. In particular, in Comparative Example 19, coloration was violent; in Comparative Examples 21-23, deformation of film was violent; and in each case, the appearance was inferior.

EXAMPLES 34-45

Oxygen-permeability test was conducted in the same manner as in Examples 16-25, except that the test was

conducted at high humidity. The results obtained are shown in Table 5 which indicate superior gas barrier property.

COMPARATIVE EXAMPLES 25 and 26

Oxygen-permeability test was conducted at high humidity as in Examples 34-45 by using an ethylene-vinyl alcohol copolymer film (trade name: Eval EF-F, manufactured by Kuraray Co., Ltd., film thickness 15 μm) which is a commercially available barrier film. The results obtained are shown in Table 5 which indicate inferior gas barrier property.

COMPARATIVE EXAMPLES 27-29

A coated film solely composed of the inorganic laminar compound was laminated and the oxygen-permeability test was conducted in the same manner as in Comparative Example 4, except that a biaxially oriented polypropylene film (opp20) was used as the substrate, inorganic laminar compounds shown in Table 6 were used, and a concentration of the inorganic laminar compound dispersion (Liquid A) was 2% by weight.

All the results obtained indicate inferior gas barrier property and inferior film-formability.

TABLE 1

	Substrate	Resin composition			Oxygen-permeability (cc/m ² /day/atm)		Reduced value (composition thickness: 1 μm)	Remarks (appearance, etc.)
		Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Film thickness (nm)	Measurement conditions	Value found	
Example 1	TAC76	PVA210	NaTs	3/7	870	31° C., 61% RH	0.092	0.08
Example 2	TAC76	HEC	NaTs	3/7	10000	31° C., 61% RH	0.185	1.85
Example 3	TAC76	PVA210	NaTs	3/7	28.4	31° C., 61% RH	5.94	0.16
Example 4	OPS25	PAV210	NaTs	3/7	24.3	31° C., 61% RH	2.13	0.05
Comp. Ex. 1	TAC76	PVA210	—	0/10	2000	31° C., 61% RH	240.6	481.2
Comp. Ex. 2	TAC76	HEC	—	0/10	10000	31° C., 61% RH	1829	18290
Comp. Ex. 3	TAC76	PVA210	Laponite	3/7	3200	31° C., 61% RH	4.72	15.1
Comp. Ex. 4	TAC76	—	NaTs	10/0	—	31° C., 61% RH	—	—
Comp. Ex. 5	TAC76	—	—	—	—	31° C., 61% RH	833.3	—
Comp. Ex. 6	OPS25	—	—	—	—	31° C., 61% RH	10284	—

TABLE 2

	Substrate	Resin composition			Oxygen-permeability (cc/m ² /day/atm)		Reduced value (composition thickness: 1 μm)	Remarks (appearance, etc.)
		Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Film thickness (nm)	Measurement conditions	Value found	
Example 5	OPET25	PVA117H	Kunipia F	1/9	348	31° C., 61% RH	0.17	0.06
Example 6	OPET25	PVA117H	"	2/8	554	31° C., 61% RH	0.05	0.027

TABLE 2-continued

Substrate	Resin composition				Oxygen-permeability (cc/m ² /day/atm)			Remarks (appearance, etc.)
	Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Film thickness (nm)	Measurement conditions	Value found	Reduced value (composition thickness: 1 μ m)	
Example 7	OPET25	PVA117H	—	3/7	587	31° C., 61% RH	<0.05	<0.029
Example 8	OPET25	PVA117H	—	5/5	594	31° C., 61% RH	0.05	0.029
Example 9	OPET25	PVA110	Smecton SA	3/7	440	23° C., 78% RH	2.88	1.26
Example 10	OPET25	PVA110	NaTs	3/7	120	23° C., 78% RH	0.92	0.11
Example 11	OPET12	PVA103	Smecton SA	2/8	375	31° C., 61% RH	1.32	0.495
Example 12	OPET12	PVA103	Kunipia F	2/8	335	31° C., 61% RH	0.20	0.067
Example 13	ONy15	PVA117H	—	3/7	769	31° C., 61% RH	<0.05	<0.038
Example 14	OPP20	PVA117H	—	2/8	506	31° C., 61% RH	0.06	0.03
Example 15	OPET12	PVA124	—	2/8	525	31° C., 61% RH	0.24	0.13
Com. Ex. 7	OPET25	PVA110	—	—	520	23° C., 78% RH	11.69	6.07
Com. Ex. 8	OPET12	PVA103	Laponite	2/8	362	31° C., 61% RH	4.48	3.62
Com. Ex. 9	ONy15	PVA117H	—	—	1450	31° C., 61% RH	2.74	3.97
Com. Ex. 10	OPET12	PVA124	—	—	1104	31° C., 61% RH	2.12	2.34
Com. Ex. 11	OPET12	—	—	—	—	31° C., 61% RH	155.6	—
							film	Substrate
Com. Ex. 12	ONy15	—	—	—	—	31° C., 61% RH	50.6	—
							film	Substrate
Com. Ex. 13	OPP20	—	—	—	—	20° C., 0% RH	1500	—
							film	Substrate

TABLE 3

Substrate	Resin composition				Cross-linking	Heat-treating conditions	Hot-water immersion conditions	Oxygen-permeability (cc/m ² /day/atm)	
	Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Film thickness (nm)				Conditions	Value found
Example 16	OPET25	PVA117H	NaTs	3/7	382	—	—	31° C., 61% RH	0.09
Example 17	OPET25	PVA117H	NaTs	3/7	382	—	—	31° C., 61% RH	8.25
Example 18	OPET25	PVA117H	NaTs	3/7	382	—	100° C., 10 min	60° C., 13 hr	31° C., 61% RH 6.47
Example 19	OPET25	PAV117H	NaTs	3/7	382	—	150° C., 10 min	60° C., 13 hr	31° C., 61% RH 0.46
Example 20	OPET25	PVA117H	NaTs	3/7	382	—	180° C., 10 min	60° C., 13 hr	31° C., 61% RH 0.37
Example 21	OPET25	PVA117H	NaTs	3/7	572	AZC	—	31° C., 61% RH	<0.05
Example 22	OPET25	PVA117H	NaTs	3/7	572	AZC	—	60° C., 13 hr	31° C., 61% RH 0.28
Example 23	OPET25	PVA117H	NaTs	3/7	572	AZC	100° C., 10 min	60° C., 13 hr	31° C., 61% RH 0.09
Example 24	OPET25	PVA117H	NaTs	3/7	572	AZC	150° C., 10 min	60° C., 13 hr	31° C., 61% RH 0.05
Example 25	OPET25	PAV117H	NaTs	3/7	572	AZC	180° C., 10 min	60° C., 13 hr	31° C., 61% RH <0.05
Comp. Ex. 14	OPET25	PVA117H	—	0/10	263	—	—	60° C., 13 hr	31° C., 61% RH 63.06
Comp. Ex. 15	OPET25	PVA117H	—	0/10	263	—	180° C., 10 min	60° C., 13 hr	31° C., 61% RH 32.82

TABLE 4

	Resin composition				Film thickness (μ m)	Dissolution resistance test (Hot water immersion: 80° C., 10 min)		Remarks (Appearance, etc.)
	Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Cross-linking agent		Heat-treating conditions	Weight percentage of remainder (wt %)	
Example 26	PVA117H	Kunipia F	3/7	—	20	80° C., 10 min	80.0	
Example 27	PVA117H	—	3/7	—	20	100° C., 10 min	80.4	
Example 28	PVA117H	—	3/7	—	20	150° C., 10 min	92.1	
Example 29	PAV117H	—	3/7	—	20	180° C., 10 min	96.6	
Example 30	PVA117H	—	3/7	AZC	20	80° C., 10 min	91.9	
Example 31	PVA117H	—	3/7	AZC	20	100° C., 10 min	93.7	
Example 32	PVA117H	—	3/7	AZC	20	150° C., 10 min	98.7	

TABLE 4-continued

TABLE 4—Continued								
Resin composition					Film thickness (μm)	Dissolution resistance test (Hot water immersion: 80° C., 10 min)		Remarks (Appearance, etc.)
Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Cross-linking agent	Heat-treating conditions		Weight percentage of remainder (wt %)		
Example 33	PVA117H	"	3/7	AZC	20	180° C., 10 min	100	Brown, large deformation
Comp. Ex. 16	PVA117H	—	0/10	—	20	—	0 (Completely dissolved)	
Comp. Ex. 17	PVA117H	—	0/10	—	20	80° C., 10 min	0 (Completely dissolved)	
Comp. Ex. 18	PVA117H	—	0/10	—	20	100° C., 10 min	0 (Completely dissolved)	
Comp. Ex. 19	PAV117H	—	0/10	—	20	150° C., 10 min	0 (Completely dissolved)	
Comp. Ex. 20	PVA117H	—	0/10	—	20	180° C., 10 min	81.3	
Comp. Ex. 21	PVA117H	—	0/10	AZC	20	80° C., 10 min	77.6	
Comp. Ex. 22	PVA117H	—	0/10	AZC	20	100° C., 10 min	88.1	
Comp. Ex. 23	PVA117H	—	0/10	AZC	20	150° C., 10 min	97.9	
Comp. Ex. 24	PVA117H	—	0/10	AZC	20	180° C., 10 min	96.5	

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Note to Tables 1 to 4
Substrate

TAC76: Triacetylcellulose (trade name: FUJITAC CLEAR, manufactured by Fuji Photo Film Co., Ltd.), surface-saponified product, film thickness: 76 μm

OPS25: Biaxially oriented polystyrene film (trade name: Styrofilm (TH) CO, manufactured by Asahi Chemical Industry Co., Ltd.), corona-treated on one side, film thickness: 25 μm

OPET25: Biaxially oriented polyethylene terephthalate film (trade name: Lumilar, manufactured by Toray Industries, Inc.), corona-treated on one side, film thickness: 25 μm

OPET12: Biaxially oriented polyethylene terephthalate film (trade name: Lumilar, manufactured by Toray Industries, Inc.), corona-treated on one side, film thickness: 12 μm

ONy15: Biaxially oriented nylon film (trade name: Emblem ON, manufactured by Unitika Ltd.), corona-treated on one side, film thickness: 15 μm

OPP20: Biaxially oriented polypropylene film (trade name: Pyren Film-OT, manufactured by Toyobo Co., Ltd.), corona-treated on one side, film thickness: 20 μm

Resin

PVA210: Polyvinyl alcohol (trade name: Poval 210, manufactured by Kuraray Co., Ltd.), saponification degree: 88.5 mole %, polymerization degree: 1,000

HEC: Hydroxyethylcellulose (manufactured by Wako Junyaku Kogyo)

PVA117H: Polyvinyl alcohol (trade name: Poval 117H, manufactured by Kuraray Co., Ltd.), saponification degree: 99.6 mole %, polymerization degree: 1,700

PVA110: Polyvinyl alcohol (trade name: Poval 110, manufactured by Kuraray Co., Ltd.), saponification degree: 98.5%, polymerization degree: 1,000

PVA103: Polyvinyl alcohol (trade name: Poval 103, manufactured by Kuraray Co., Ltd.), saponification degree: 98.5%, polymerization degree: 300

PVA124: Polyvinyl alcohol (trade name: Poval 124, manufactured by Kuraray), saponification degree: 98.5%, polymerization degree: 2,400

30 Inorganic laminar compound

NaTs: Synthetic tetrasilic mica (trade name: NaTs, manufactured by Topy Kogyo), particle size: 977 nm, a value: 0.9557 nm, aspect ratio: 1043

35 Laponite: Synthetic hectorite (trade name: Laponite XLG, manufactured by Nippon Silica Kogyo), particle size: 35 nm, a value: about 1 nm (diffraction peak: broad), aspect ratio: about 35

KunipiaF: High purity montmorillonite (trade name: KunipiaF, manufactured by Kunimine Kogyo), particle size: 560 nm, a value: 1.2156 nm, aspect ratio: 461

SmectonSA: Synthetic saponite (trade name: SmectonSA, manufactured by Kunimine Kogyo), particle size: 108 nm, a value: about 1 nm (diffraction peak: broad), aspect ratio: about 108

45 Cross-linking agent

AZC: Ammonium zirconium carbonate (trade name: ZircosolAC-7, manufactured by Daiichi Kigenso Kogyo), aqueous solution containing 15% by weight of zirconium oxide, added so that the amount of hydrogen-bonding group in the resin became 15 moles per mole of zirconium element.

TABLE 5

		Oxygen-permeability (cc/m ² /day/atm)			
Sample	Heat-treating conditions	Measurement conditions	Value found	Reduced value per μm	
Example 34	Example 16	—	23.9° C., 90.8% RH	0.37	0.14
Example 35	"	150° C., 10 min	"	0.41	0.16
Example 36	"	180° C., 10 min	"	0.21	0.10
Example 37	Example 21	—	"	0.36	0.20
Example 38	"	150° C., 10 min	"	0.13	0.07
Example 39	"	180° C., 10 min	"	0.10	0.06
Example 40	Example 16	—	23.8° C., 94.5% RH	1.01	0.38
Example 41	"	150° C., 10 min	"	0.80	0.30

TABLE 5-continued

Sample	Heat-treating conditions	Measurement conditions	Oxygen-permeability (cc/m ² /day/atm)	
			Value found	Reduced value per μ m
Example 42	180° C., 10 min	"	0.66	0.25
Example 43	—	"	0.65	0.37
Example 44	150° C., 10 min	"	0.18	0.10
Example 45	180° C., 10 min	"	0.11	0.06
Comp. Ex. 25	EVOH-F	23.9° C., 90.8% RH	5.0	75
Comp. Ex. 26	—	23.8° C., 94.5% RH	6.5	97.5

EVOH-F: Ethylene-vinylalcohol copolymer (trade name, Eval-EF-F, mfd. by Kuraray Co., Ltd.; thickness 15 μ m)

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TABLE 6

Kind of	Oxygen-permeability			Remarks (appearance, etc.)
	Value found (cc/m ² /day/atm)	Product of Thickness of the dried layer and Value found (cc · μ m/m ² /day/atm)		
inorganic laminar compound [Thickness of the dried layer]				
Comp. Ex. 27	NaTs [5 μ m]	2000	10000	Blanching
Comp. Ex. 28	Kunipia F [7 μ m]	550	3850	Blanching
Comp. Ex. 29	Smecton SA [20 μ m]	1050	21000	A little opaque white

What is claimed is:

1. A resin composition comprising a high hydrogen-bonding resin containing from 20 wt % to 60 wt % of a hydrogen-bonding group or ionic group based on a total weight of the hydrogen-bonding resin, and a non-film-forming clay mineral having a swellability, the resin composition having a volume ratio of the clay mineral to the hydrogen-bonding resin in the range of 5:95 to 90:10, wherein the clay mineral has an aspect ratio of in a range of from 50 to 5000.

2. The resin composition according to claim 1, wherein the aspect ratio of the clay mineral is in a range of from 200 to 3,000.

3. The resin composition according claim 1, wherein the weight percentage of the hydrogen-bonding group or ionic group per unit weight of the hydrogen-bonding resin is in the range of 30–50%.

4. The resin composition according to claim 1, wherein the high hydrogen-bonding resin is polyvinyl alcohol or a polysaccharide.

5. The resin composition according to claim 1, which further contains a cross-linking agent for the hydrogen-bonding group of the hydrogen-bonding resin.

6. The resin composition according to claim 5, wherein the cross-linking agent is a compound containing zirconium.

7. A laminated film or laminate having at least one layer formulated from the composition claimed in claim 1, 2, 3, 4, 5, or 6.

8. A laminated film or laminate comprising:

at least one layer selected from the group consisting of a biaxially oriented polypropylene film, a biaxially ori-

ented nylon film and a biaxially oriented polyethylene terephthalate film; and

at least one layer formulated from the composition claimed in claim 1, 2, 3, 4, 5, or 6.

9. The resin composition according to claim 1, wherein the clay mineral is selected from the group consisting of montmorillonite, hectorite, sodium terasillic mica, sodium taeniolite, and any combination thereof.

10. A water-resistant gas-barrier film formulated at least from a resin composition, said resin composition comprising a high hydrogen-bonding resin containing from 20 wt % to 60 wt % of a hydrogen-bonding group or ionic group based on a total weight of the hydrogen-bonding resin, and a non-film-forming clay mineral having a swellability, the resin composition having a volume ratio of the clay mineral to the hydrogen-bonding resin in the range of 5:95 to 90:10 wherein the clay mineral has an aspect ratio of in a range of from 50 to 5000.

11. A water-resistant gas-barrier film according to claim 10, wherein the aspect ratio of the clay mineral is in a range of from 200 to 3,000.

12. A water-resistant gas-barrier film according to claim 10, wherein the weight percentage of the hydrogen-bonding group or ionic group per unit weight of the hydrogen-bonding resin is in the range of 30–50%.

13. A water-resistant gas-barrier film according to claim 10, wherein the high hydrogen-bonding resin is polyvinyl alcohol or a polysaccharide.

14. A water-resistant gas-barrier film according to claim 10, which further contains a cross-linking agent for the hydrogen-bonding group of the hydrogen-bonding resin.

15. A water-resistant gas-barrier film according to claim 14, wherein the cross-linking agent is a compound containing zirconium.

16. A water-resistant gas-barrier film according to claim 10, wherein the film has an oxygen permeability per μ m of thickness at 31° C. and 61% RH of 2 cc/m²/day/atm or less.

17. A water-resistant gas-barrier film according to claim 10, wherein the film has an oxygen permeability per μ m of thickness at 31° C. and 61% RH of 0.2 cc/m²/day/atm or less.

18. A water-resistant gas-barrier film according to claim 10, wherein the clay mineral is selected from the group consisting of montmorillonite, hectorite, sodium terasillic mica, sodium taeniolite, and any combination thereof.

* * * * *



US005969029A

United States Patent [19]

Kotani et al.

[11] **Patent Number:** **5,969,029**[45] **Date of Patent:** **Oct. 19, 1999**[54] **PROCESS FOR PRODUCING A GAS BARRIER RESIN COMPOSITION**[75] **Inventors:** Kozo Kotani, Toyonaka; Toshio Kawakita; Taiichi Kawakita, both of Ibaraki; Toshiya Kuroda, Takatsuki, all of Japan[73] **Assignee:** Sumitomo Chemical Company, Limited, Osaka, Japan[21] **Appl. No.:** 08/951,303[22] **Filed:** Oct. 16, 1997**Related U.S. Application Data**

[60] Division of application No. 08/410,380, Apr. 4, 1995, Pat. No. 5,700,560, which is a continuation-in-part of application No. 08/384,798, Feb. 6, 1995, abandoned, which is a continuation of application No. 08/097,889, Jul. 28, 1993, abandoned.

[30] **Foreign Application Priority Data**

Jul. 29, 1992 [JP] Japan 4-202339

[51] **Int. Cl.⁶** C08K 3/34[52] **U.S. Cl.** 524/447; 524/443[58] **Field of Search** 524/443, 447[56] **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—Paul R. Michl*Attorney, Agent, or Firm*—Pillsbury Madison & Sutro LLP[57] **ABSTRACT**

A gas barrier resin composition or its film having very high level gas barrier and moisture barrier properties, which includes at least a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound having a particle size of 5 μm and an aspect ratio of 50–5,000. The resin composition or its film can be produced by dispersing a non-film-forming inorganic laminar compound in a high hydrogen-bonding resin or resin solution in such a state that the non-film-forming inorganic laminar compound is swollen or cloven with a solvent, and removing the solvent from the dispersion, if necessary in the form of a film, while maintaining the state.

4 Claims, 7 Drawing Sheets

FIG. 1

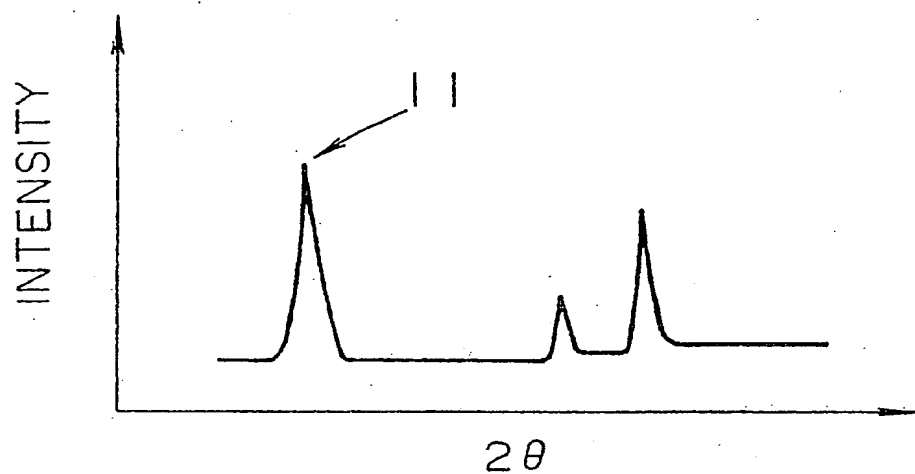


FIG. 2

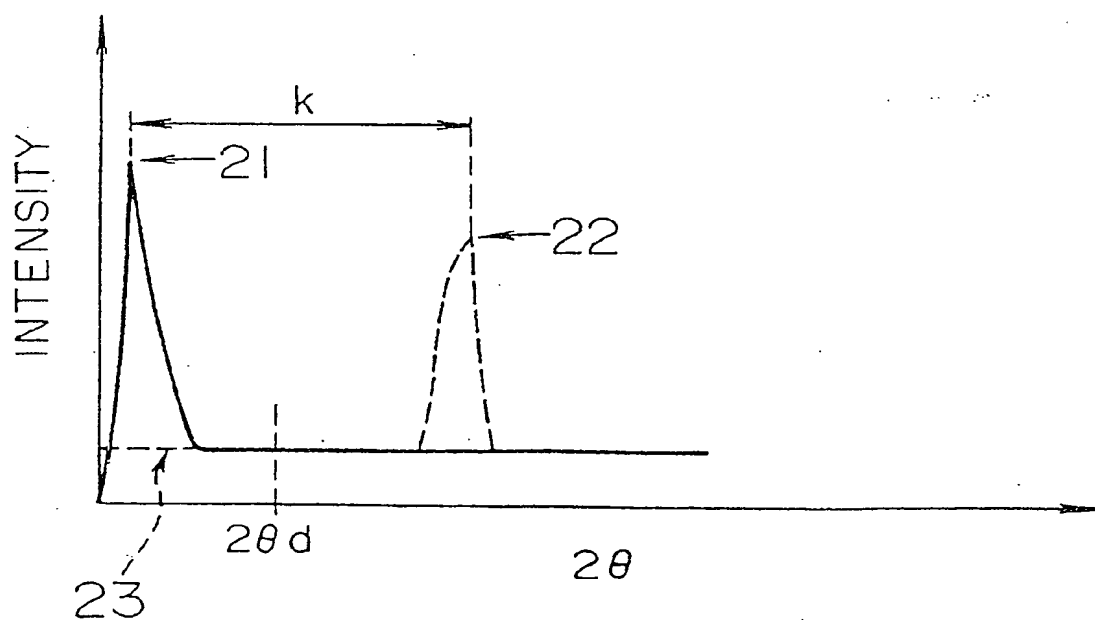


FIG. 3

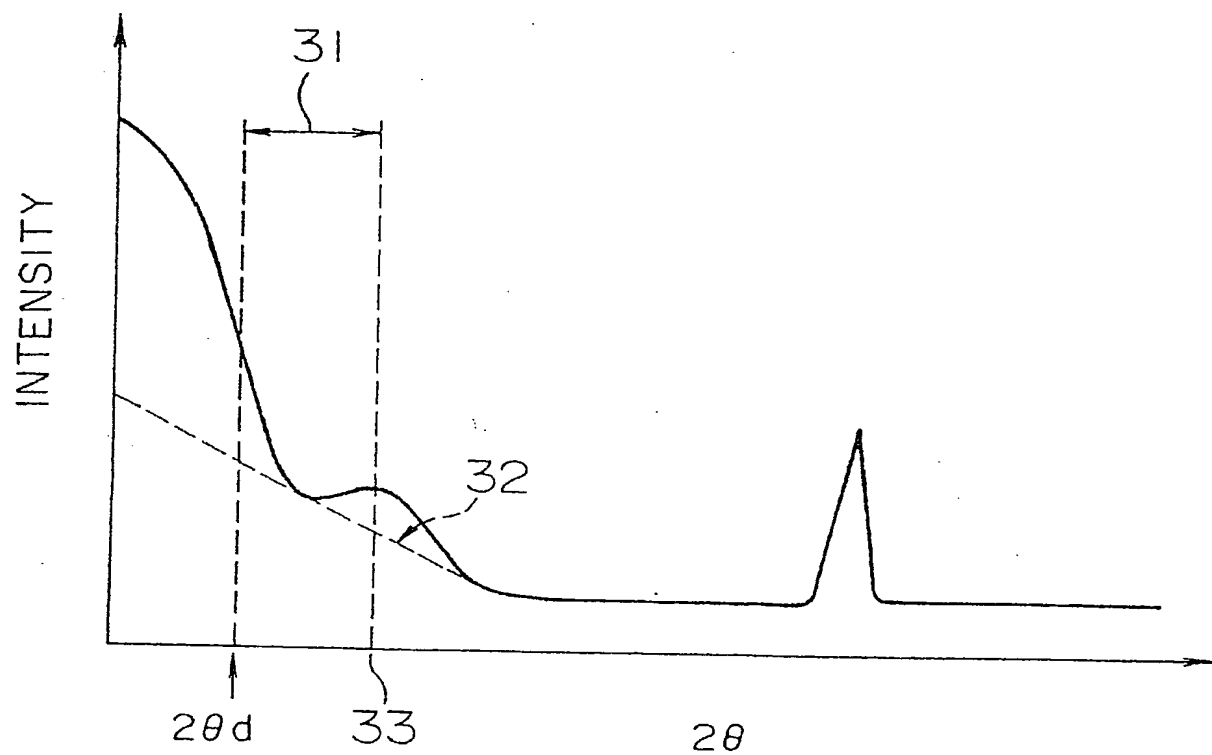


FIG. 4

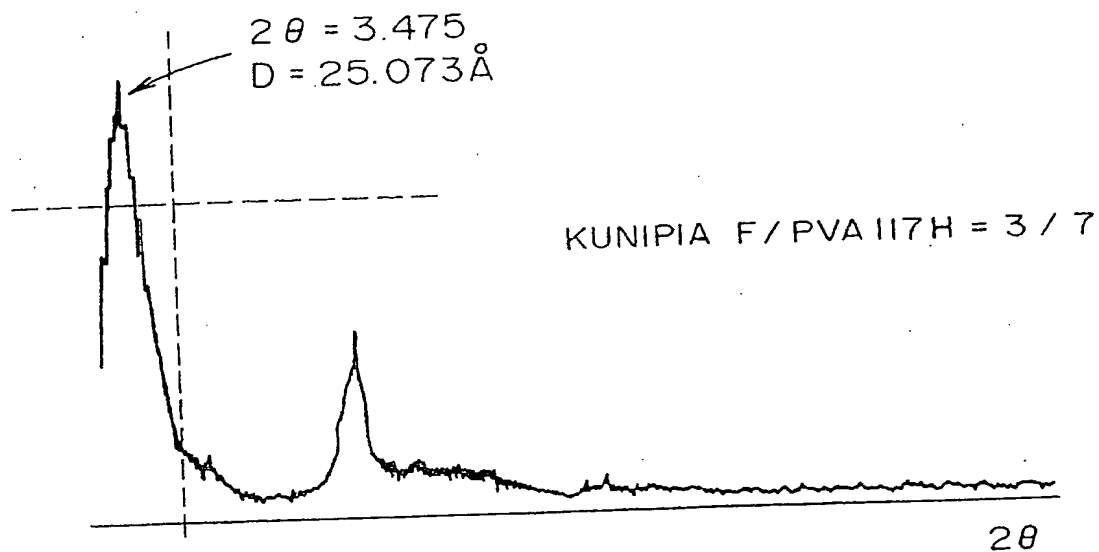


FIG. 5

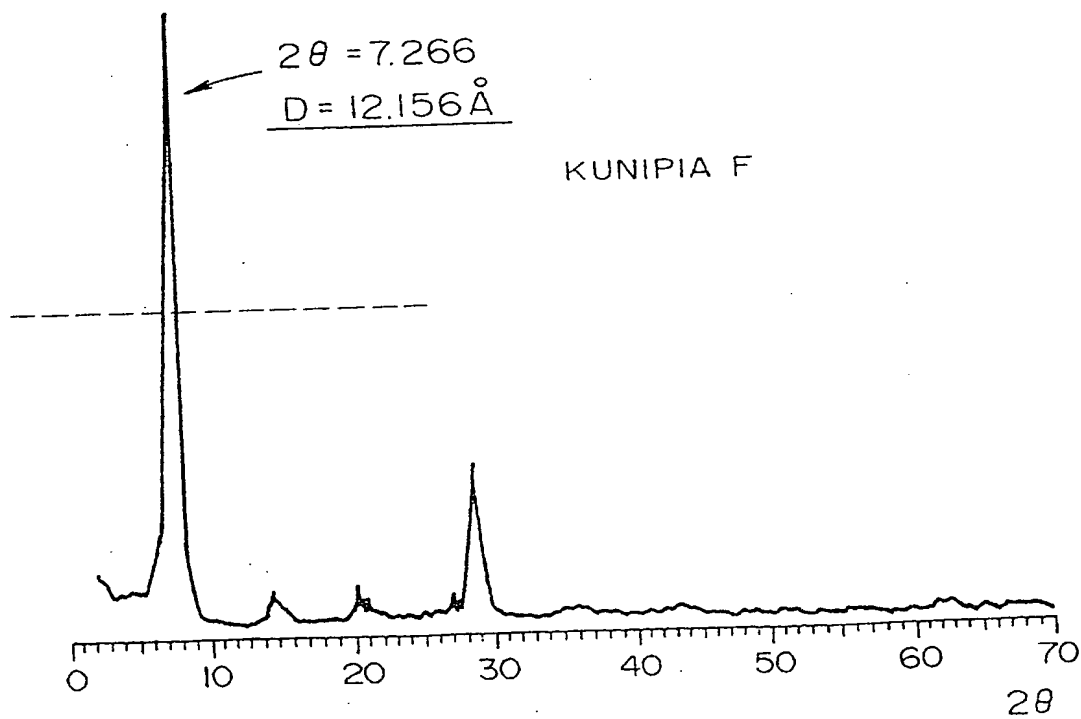


FIG. 6

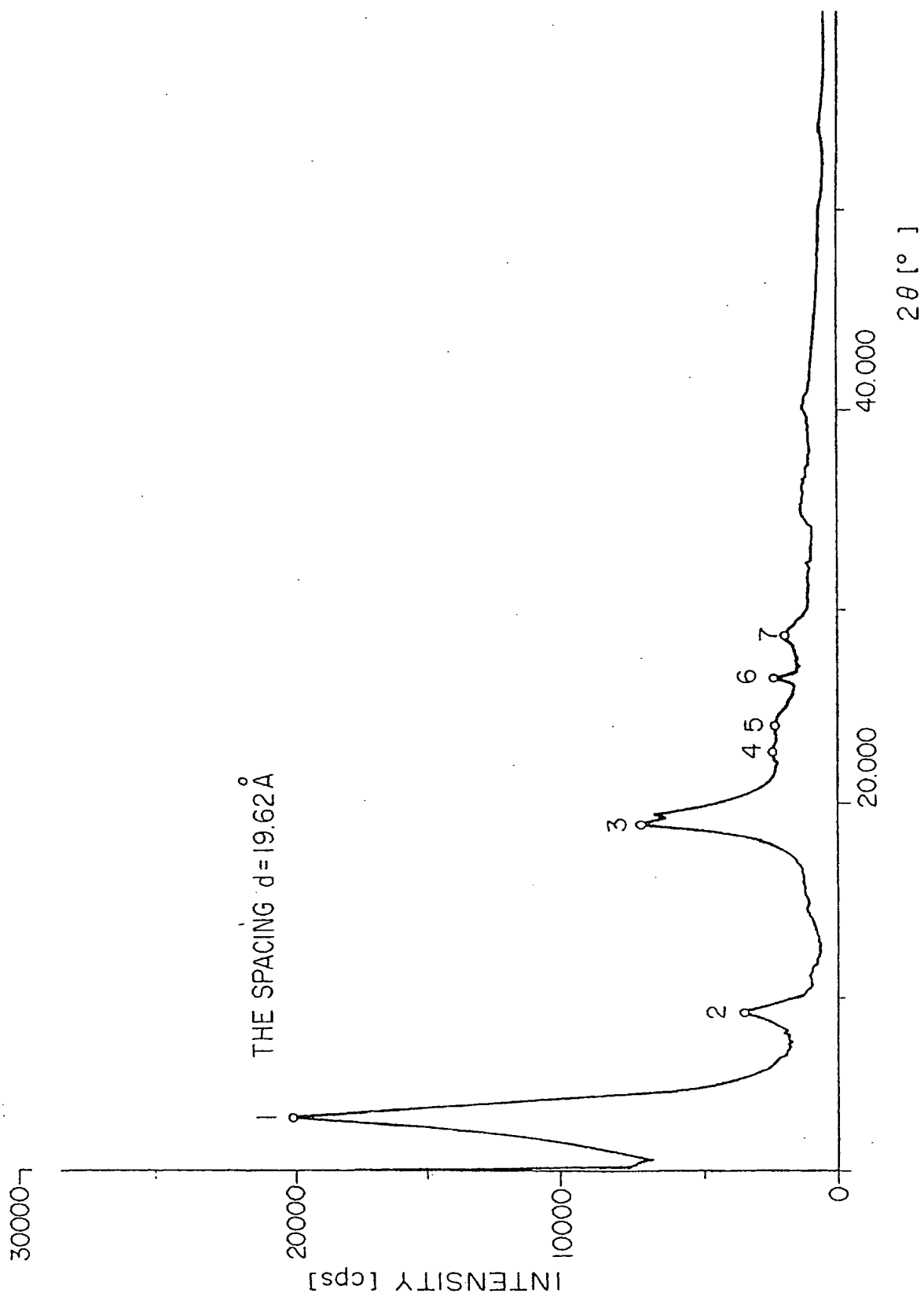


FIG. 7

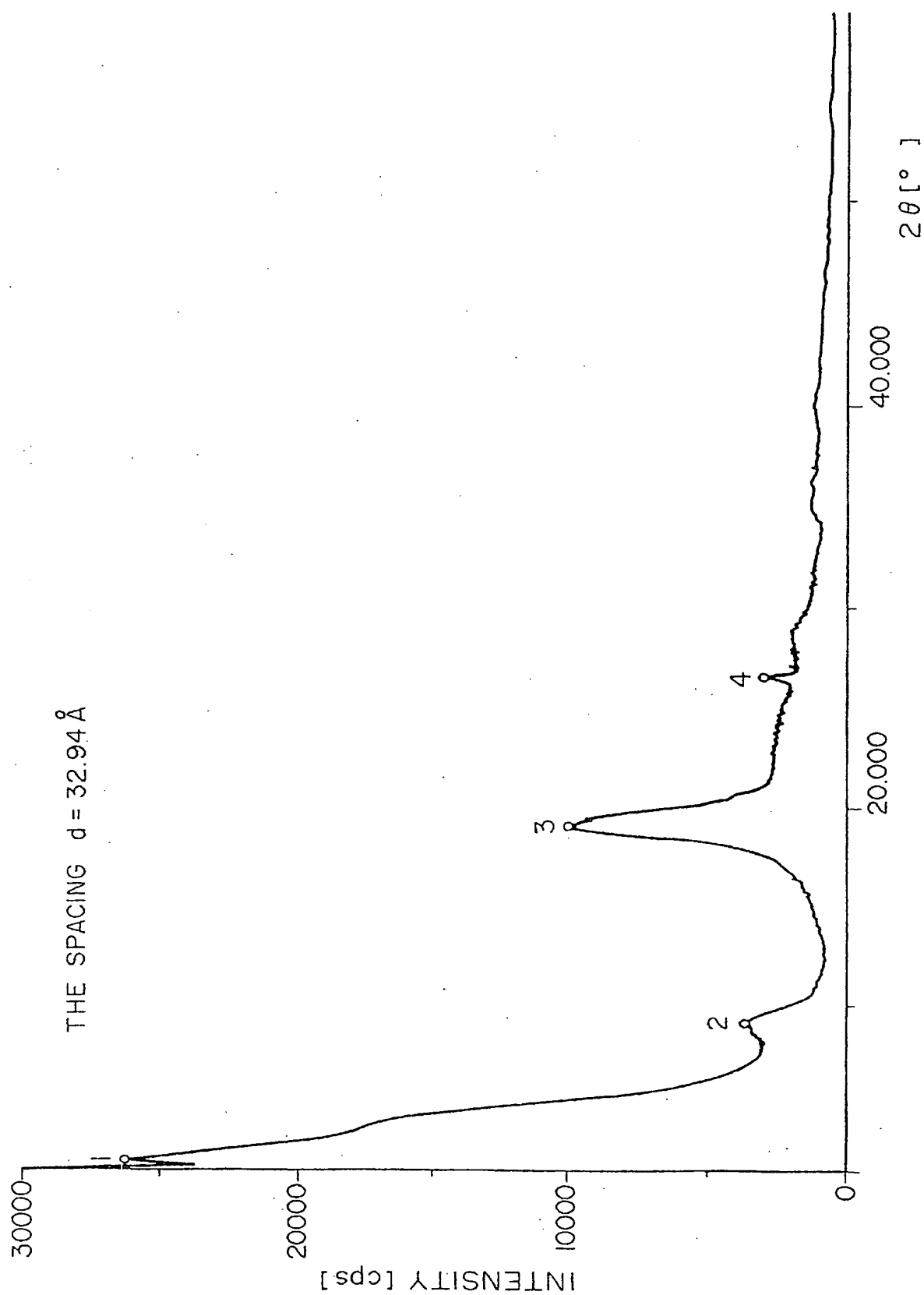


FIG. 8

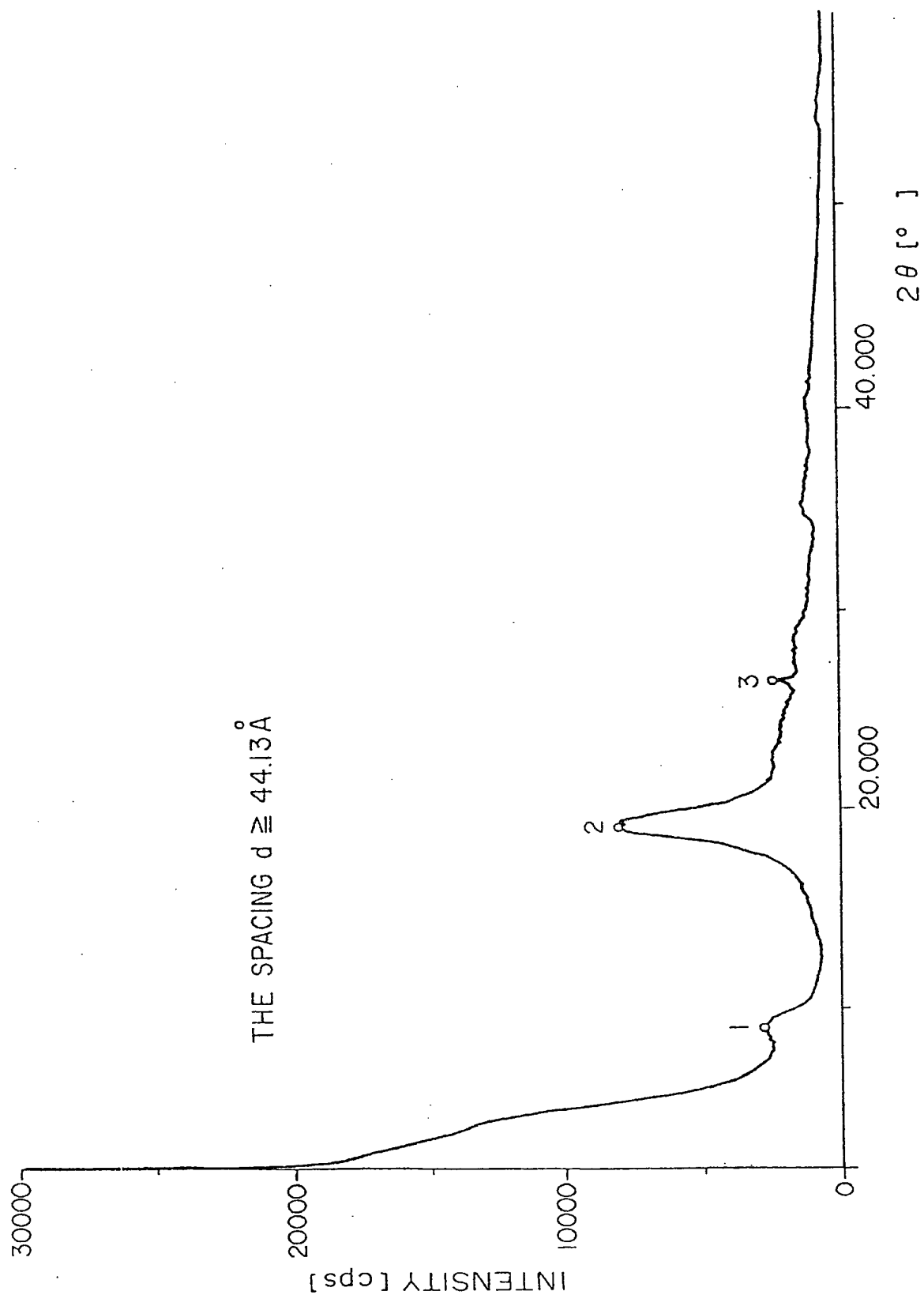
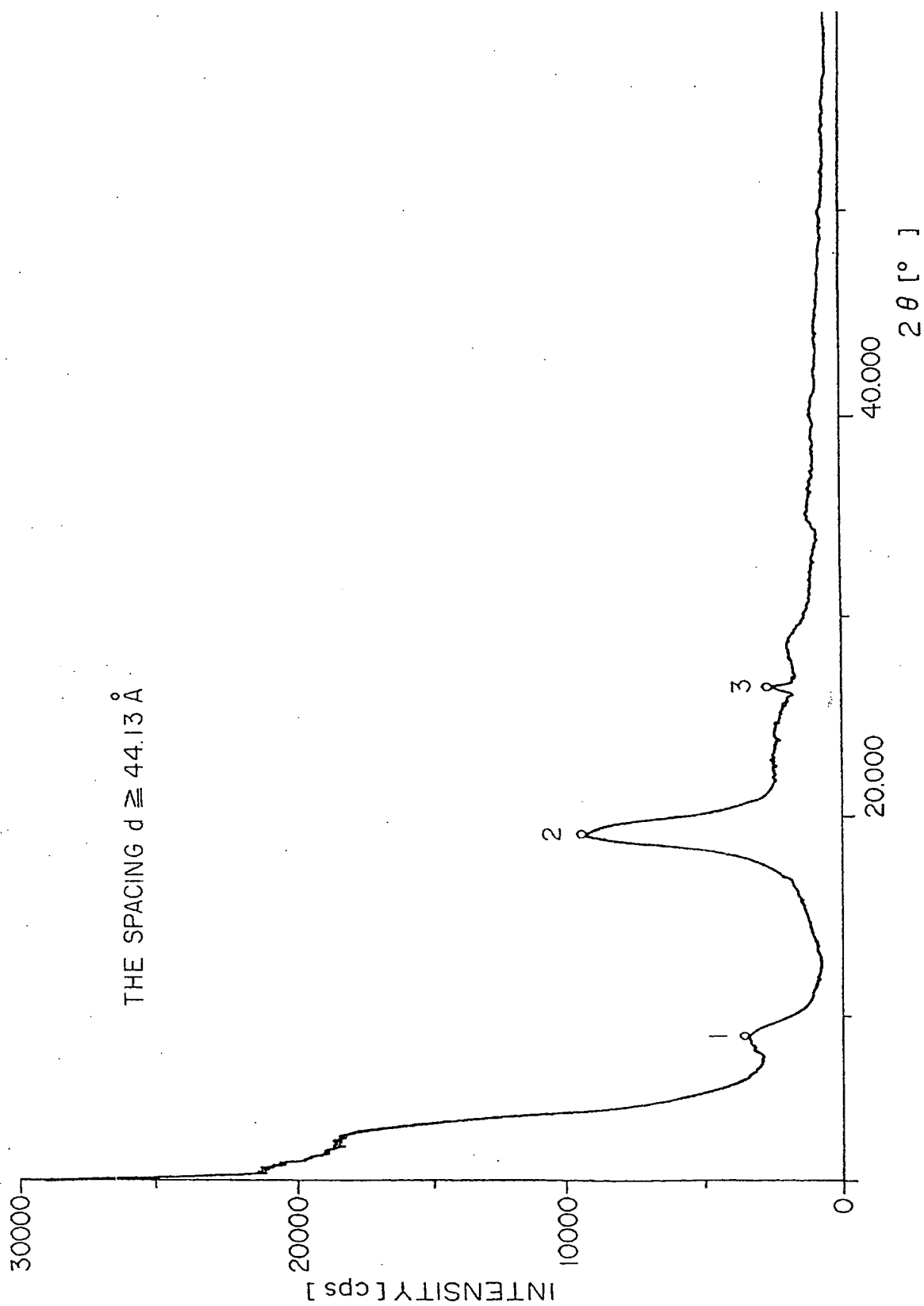


FIG. 9



PROCESS FOR PRODUCING A GAS BARRIER RESIN COMPOSITION

CROSS-REFERENCES TO RELATED APPLICATIONS

This is a division of application Ser. No. 08/416,380, filed Apr. 4, 1995, 5,700,560, which is a Continuation-in-part of application Ser. No. 08/384,798, filed Feb. 6, 1995, abandoned, which is a Continuation of application Ser. No. 08/097,889, filed Jul. 28, 1993, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a resin composition, film or laminate excellent in gas barrier properties and to a process for producing the same.

2. Description of the Related Art

Many functions are required for packaging, including adequate gas barrier properties for protecting the package contents. Gas barrier properties are important properties which affect the preservability of foods. Change in distributive systems, diversification of packaging techniques, additive regulations and change in taste increase more and more the necessity for adequate gas barrier properties. However, the gas barrier properties have been weak points of general plastics.

The food-deteriorating factors are oxygen, light, heat, water and the like, and in particular, oxygen is a serious factor. Gas barrier materials are indispensable for effectively intercepting oxygen and simultaneously for controlling the deterioration of foods such as gas-filling, vacuum packaging and the like. Since the barrier materials have a barrier function to not only oxygen gas but also other various gases, organic solvent vapors, fragrance and the like, they can be used for anticorrosion, deodorization and antisublimation and have been utilized in many fields of foods, cosmetics, agricultural chemicals, pharmaceuticals and the like such as confectionery, bonito pack, retort pouch, mineral water container and the like.

Of films consisting of a thermoplastic resin, oriented films of polypropylene, polyester, polyamide or the like have excellent mechanical properties, heat resistance, transparency and the like and are widely used as packaging materials. However, when these films are used for packaging foods, they are unsatisfactory in barrier properties to oxygen and other gases, and therefore, they tend to cause such various problems insofar as their contents become deteriorated by oxidative degradation or with aerobic bacteria, fragrant components permeate the films to lose the taste of the contents, and the moisture in the atmosphere wets the contents to make the taste bad. Thus, usually, such a measure is often taken that other film layers having good gas barrier properties are laminated thereto.

Heretofore, various transparent plastic materials having unsatisfactory gas barrier properties have been known and there are, for example, films composed of polyvinyl alcohol, ethylene-vinyl alcohol copolymer or polyvinylidene dichloride resin. However, these plastic materials are oxygen-permeable in such a degree that the amount of oxygen permeated cannot be neglected while a metal or glass material to be used in canning or bottling has an oxygen permeability of substantially zero.

Another method for imparting gas barrier properties is a method of dispersing an inorganic material in the flat form in a resin. For example, Japanese Patent Application Kokai

No. 62-148,532 describes a production method which comprises coating on a releasable substrate a coating composition consisting of 100 parts by weight of a polyurethane resin solution having a concentration of 30% in 1,6-hexanepolycarbonate diol, 25 parts by weight of mica powder and 60 parts by weight of dimethyl-formamide, drying the same and then releasing it from the substrate.

Japanese Patent Application Kokai No. 64-043,554 describes a method of obtaining a film which comprises adding mica particles having an average length of 7 μ m and an aspect ratio of 140 to a methanolic aqueous solution of an ethylene-vinyl alcohol copolymer, pouring the solution in a cold water to form a precipitate, removing the precipitate by filtration, drying it to form pellets and then forming the pellets into a film.

Further, Japanese Patent Application Kokai No. 3-93,542 describes a method which comprises coating a biaxially oriented polyethylene terephthalate (OPET) film with a coating composition consisting of a silyl group-containing modified polyvinyl alcohol and synthetic hectorite at a weight ratio of 50:50, drying the same and then heat-treating it at 130-150° C.

However, the films obtained by these techniques are still not sufficient in gas barrier properties and cannot always be said to be satisfactory.

SUMMARY OF THE INVENTION

In order to solve the above-mentioned problems, the present inventors have made extensive research to find that a resin composition consisting of a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound can be given excellent gas barrier properties by increasing the aspect ratio of the non-film-forming inorganic laminar compound.

An object of this invention is to provide a gas barrier resin composition or its molded article including a film having high level gas barrier and moisture barrier properties.

Another object of this invention is to provide a process for producing the gas barrier resin composition or its molded article including a film.

Other objects and advantages of this invention will become apparent from the following description.

According to this invention, there is provided a resin composition or its film or laminate comprising a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound having a particle size of 5 μ m or less and an aspect ratio of 50 to 5,000.

This invention further provides a process for producing the above resin composition or its film, which comprises dispersing a non-film-forming inorganic laminar compound in a high hydrogen-bonding resin or resin solution in the state that the non-film-forming inorganic laminar compound is swollen or cloven with a solvent, and removing the solvent from the dispersion, if necessary in the form of a film, while keeping said state.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph typically showing a relationship between X-ray diffraction peaks of an inorganic laminar compound and "the unit thickness a" of the inorganic laminar compound. In FIG. 1, 11 indicates the peak which corresponds to "the unit thickness a" of the inorganic laminar compound.

FIG. 2 is a graph typically showing a relationship between X-ray diffraction peaks of a resin composition containing an inorganic laminar compound and "the spacing dd" of the

resin composition. In FIG. 2, 21 indicates the peak which corresponds to "the spacing d " of the resin composition, 22 indicates a position of the peak which corresponds to "the unit thickness a " of the inorganic laminar compound, 23 indicates the base line, k value, when it is converted into a length, and is not less than the width of one chain of the resin, and θ_d is a diffraction angle which corresponds to the sum of the unit thickness a and the width of one chain of the resin.

FIG. 3 is a graph typically showing a relationship between X-ray diffraction peaks of a resin composition and "the spacing d " of the resin composition when the detection of the peak which corresponds to the spacing d is disturbed by being overlapped with a halo (or background). In FIG. 3, the peak which corresponds to the spacing d is defined by the peak of the area from which the part below the base line at the angle range of lower than $2\theta_d$ is removed. 31 indicates the width of one chain of the resin, 32 indicates the base line, and 33 indicates the peak which corresponds to "the unit thickness a " of the inorganic laminar compound.

FIG. 4 is a graph showing X-ray diffraction peaks of the composition of polyvinyl alcohol, PVA-117H/Kunipia F used in Examples.

FIG. 5 is a graph showing X-ray diffraction peaks of Kunipia F used in Examples.

FIG. 6 is a graph showing X-ray diffraction peaks of the composition having the spacing d of 19.62 Å (which is a pattern in FIG. 2 as mentioned above).

FIG. 7 is a graph showing X-ray diffraction peaks of the composition having the spacing d of 32.94 Å (which is a pattern in FIG. 2 or FIG. 3 as mentioned above).

FIG. 8 is a graph showing X-ray diffraction peaks of the composition having the spacing d of 44.13 Å or more (which is a pattern in FIG. 3 as mentioned above).

FIG. 9 is a graph showing X-ray diffraction peaks of the composition having the spacing d of 44.13 Å or more (which is a pattern in FIG. 3 as mentioned above). However, in this case a clear shoulder, as compared with FIG. 8, due to the peak observed in lower angle range than the diffraction peak put a mark 1. is observed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The non-film-forming inorganic laminar compound used in this invention is an inorganic compound having a laminar structure formed by unit crystal layers being piled up on one another, and any inorganic compound may be used so long as it has a particle size of 5 μm or less and an aspect ratio of 50–5,000. In view of the gas barrier properties, the aspect ratio is preferably 200–3,000. If the aspect ratio is less than 50, the gas barrier properties are not sufficiently exhibited, and if the aspect ratio is more than 5,000, such an inorganic compound is technically difficult to produce and is too expensive.

The term "non-film-forming" used in the present invention means that the inorganic laminar compound exhibits insufficient gas barrier properties when subject to such processes as blanching of a film, exfoliation of part of a film or formation of many piercing holes in a film at the time of film-forming.

In view of easy dispersion of the inorganic laminar compound in a resin, the non-film-forming inorganic laminar compound used in the present invention preferably has 500 cc· $\mu\text{m}/\text{m}^2/\text{day}/\text{atm}$ or more of a product of a coating film thickness and oxygen-permeability measured for a film

obtained by film-forming under the conditions shown in Comparative Examples 27–29.

When the particle size is 3 μm or less, the transparency is higher and such an inorganic compound is preferred.

Specific examples of the non-film-forming inorganic laminar compound include graphite, phosphoric acid salt derivative type compounds (e.g. zirconium phosphate compounds), chalcogenides [the IV Group metal (Ti, Zr, Hf) dichalcogenides, the V Group metal (V, Nb, Ta) dichalcogenides and the VI Group metal (Mo, W) dichalcogenides which are represented by the formula MX_2 wherein X represents chalcogen (Sr Se, Te)], clay minerals and the like.

The measurement of true particle size in a resin composition is very difficult, and therefore, the particle size of the non-film-forming inorganic laminar compound used in this invention is a value determined according to a dynamic light-scattering method in a solvent.

When a non-film-forming inorganic laminar compound sufficiently swollen with the same solvent as used in the dynamic light-scattering method is compounded with a resin, the particle size of the non-film-forming inorganic laminar compound in the resin can be considered to be close to the particle size in a solvent.

The aspect ratio (Z) of the non-film-forming inorganic laminar compound used in this invention is indicated by the relation of $Z=L/a$ in which L is the particle size determined according to the dynamic light-scattering method in a solvent and a is the unit thickness of the non-film-forming inorganic laminar compound (the unit thickness a is a value determined by measurement of the non-film-forming inorganic laminar compound alone according to the powder X-ray diffraction), provided that in $Z=L/a$, the spacing d determined by the powder X-ray diffraction of the composition is present and satisfies a relation of $a < d$, in which the value of $d-a$ is required to be greater than the width of one chain of resin in the composition.

Specifically, the unit thickness a is defined by the spacing determined from an angle θ which corresponds to the peak at the lowest angle among the observed diffraction peaks, on a basis of the Bragg's Equation ($n\lambda=2D\sin\theta$, $n=1, 2, 3, \dots$) as typically shown in FIG. 1 having 2θ as a horizontal axis and an intensity of X-ray diffraction peak as a vertical axis (the details of the powder X-ray diffraction method can be referred to, for example, "Manual for Instrumental Analysis (a)", Edited by Jiro Shiokawa and Published by Kagaku Dojin, Japan, page 69, 1985).

As typically shown in FIG. 2 having 2θ as a horizontal axis and an intensity of X-ray diffraction peak as a vertical axis, the spacing d ($a < d$) is a spacing which corresponds to the peak at the lowest angle among the diffraction peaks observed in lower angle (large spacing) range than the diffraction peak which corresponds to the unit thickness a as mentioned above. As typically shown in FIG. 3, when the detection of the peak which corresponds to the spacing d as mentioned above is disturbed by being overlapped with a halo (or background), the peak which corresponds to the spacing d is defined by the peak of the area from which the part below the base line at the angle range of lower than $2\theta_d$ is removed. θ_d is herein a diffraction angle which corresponds to the sum of the unit thickness a and the width of one chain of the resin (the details of the method for determining the spacing d can be referred to, for example, "Encyclopedia of Clay", Edited by Shuichi Iwao et al., Published by Asakura Shoten, Japan, page 35 et seq. and page 271 et seq., 1985).

In this way, "integrated intensity" of the diffraction peak (which corresponds to the spacing d) observed in the powder

X-ray diffraction of the resin composition is preferably 2 or more (more preferably, 10 or more) of a relative ratio to the integrated intensity of the base diffraction peak (which corresponds to the unit thickness a).

Z cannot necessarily be said to be the true aspect ratio of the non-film-forming inorganic laminar compound in the resin composition; however, it is considerably reasonable for the following reason:

The aspect ratio of the non-film-forming inorganic laminar compound in the resin composition is very difficult to measure directly. Between the spacing d obtained by the powder X-ray diffraction of the composition and the unit thickness a determined by the powder X-ray diffraction of the non-film-forming inorganic laminar compound, there is a relation of $a < d$, and when the d - a value is greater than the width of one chain of the resin in the composition, it follows that in the resin composition, the resin is inserted between the layers of the non-film-forming inorganic laminar compound, and hence, it is clear that the thickness of the non-film-forming inorganic laminar compound is the unit thickness a .

"The width of one chain of the resin" can be determined by a simulation calculation etc. (for example, referred to "Introduction of Polymer Science", Published by Kagaku Dojin, Japan, pages 103-110, 1981). That of poly(vinyl alcohol) was determined to be 4 to 5 Å (that of water molecule determined to be 2 to 3 Å).

Also, the measurement of the true particle size in the resin composition is very difficult, and taking the case where the non-film-forming inorganic laminar compound is sufficiently swollen with the same solvent as used in the dynamic light-scattering method and then compounded with the resin, it can be understood that the particle size of the non-film-forming inorganic laminar compound in the resin is considerably close to that in the solvent, provided that the particle size L determined by the dynamic light-scattering method is considered not to exceed the long diameter L_{max} , so that the true aspect ratio L_{max}/a cannot theoretically become lower than Z in the definition of the aspect ratio in this invention.

From the above two points, it is considered that the aspect ratio in this invention be relatively high in propriety. In this invention, the aspect ratio and particle size mean the above-defined aspect ratio and particle size, respectively.

The non-film-forming inorganic laminar compound having a large aspect ratio is preferably an inorganic laminar compound which can be swollen or cloven with a solvent.

The degree of "swelling and cleavage" properties to a solvent of the inorganic laminar compound used in the present invention can be determined by the following "swelling and cleavage" tests. The swelling property of the inorganic laminar compound is preferably 5 or more (more preferably, 20 or more). This cleavage property of the inorganic laminar compound is preferably 5 or more (more preferably, 20 or more). In these cases, a solvent having a smaller density than that of the inorganic laminar compound is used as a solvent. When the inorganic laminar compound is natural swellable clay minerals, water is preferably used as the solvent.

[Swelling Test]

2 g of an inorganic laminar compound was slowly added to 100 ml of a solvent (100 ml of a measuring cylinder was used as a container). After leaving to stand at 23° C. for 24 hours, a volume of a dispersed layer of the inorganic laminar compound was measured from the scale of a boundary between the dispersed layer of the inorganic laminar compound and a supernatant liquid. The larger the value of the volume, the higher the swelling property (swellability).

[Cleavage Test]

30 g of an inorganic laminar compound was slowly added to 1500 ml of a solvent and dispersed in the solvent at a peripheral speed of 8.5 m/sec at 23° C. for 90 minutes by the use of a dispersing machine (manufactured by Asada Tekko, trade name: Desper MH-L, a diameter of an impeller blade: 52 mm, a number of agitating: 3100 rpm, a container volume: 3 l, a distance between the bottom of the container and the impeller blade: 28 mm). Thereafter, 100 ml of the dispersed solution was taken and added to a measuring cylinder, left to stand for 60 minutes, and then the volume of the dispersed layer of the inorganic laminar compound was measured from the scale of the boundary between the dispersed layer of the inorganic laminar compound and a supernatant liquid.

Among the inorganic laminar compounds which can be swollen or cloven with a solvent, non-film-forming clay minerals having a swellability are more preferable. The clay minerals are classified into a type of a two-layer structure in which on the upper portion of the tetrahedron layer of silica is present an octahedron layer in which the center metal is aluminum, magnesium or the like, and a type of a three-layer structure in which an octahedron layer in which the center metal is aluminum, magnesium or the like is sandwiched between tetrahedron layers of silica.

The former type includes the kaolinite Group, the antigorite Group and the like. The latter type includes the smectite Group, the vermiculite Group, the mica Group and the like corresponding to the number of cations between the layers.

Specifically, kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, hectorite, sodium terasilic mica, sodium taeniolite, common mica, margarite, talc, vermiculite, phlogopite, xanthophyllite, chlorite and the like.

The solvent for swelling the non-film-forming inorganic laminar compound is not critical; however, in the case of, for example, natural swellable non-film-forming clay minerals, preferable are water; alcohols such as methanol, ethanol, propanol, isopropanol, ethylene glycol, diethylene glycol and the like; dimethylformamide; dimethylsulfoxide; acetone; and the like. Water and alcohols such as methanol and the like are more preferable.

The high hydrogen-bonding resin used in this invention is not critical and includes, for example, polyvinyl alcohol (PVA), ethylene-vinyl alcohol copolymer (EVOH), polysaccharide, polyacrylic acid and its esters, and the like.

It is preferred that the high hydrogen-bonding resins satisfy the requirement that the weight percentage of hydrogen-bonding group or ionic group per unit weight of the resin falls within the range of 20-60%.

It is more preferred that the high hydrogen-bonding resins satisfy the requirement that the weight percentage of the hydrogen-bonding group or ionic group per unit weight of the resin falls within the range of 30-50%. The hydrogen-bonding group of the high hydrogen-bonding resin includes hydroxyl group, amino group, thiol group, carboxyl group, sulfonic acid group, phosphoric acid group and the like, and the ionic group includes carboxylate group, sulfonate ion group, phosphate ion group, ammonium group, sulfonium group and the like.

Of the hydrogen-bonding groups or ionic groups of the high hydrogen-bonding resins, more preferable are hydroxyl group, amino group, carboxyl group, sulfonic acid group, carboxylate group, sulfonate ion group, ammonium group and the like.

Specific examples of the high hydrogen-bonding resin include, for example, polyvinyl alcohol, ethylene-vinyl alco-

hol copolymer, the vinyl alcohol fraction of which is 41 mole % or more, polysaccharide such as hydroxymethylcellulose, hydroxyethylcellulose, carboxymethylcellulose, amylose, amylopectin, pluran, cardran, xanthan, chitin, chitosan, cellulose and the like; polyacrylic acid; polysodium acrylate; polybenzenesulfonic acid; polysodium benzenesulfonate, polyethyleneimine; polyallylamine; its ammonium salt; polyvinyl thiol; polyglycerin; and the like.

More preferable high hydrogen-bonding resins are soluble resins in solvents which can swell and cleave the inorganic laminar compound, such as polyvinyl alcohol and polysaccharide etc.

The term "polyvinyl alcohol" referred to herein means a polymer having a monomer unit of vinyl alcohol as a main component. Such a "polyvinyl alcohol" includes, for example, a polymer obtained by hydrolyzing or ester interchanging (saponifying) the acetate ester portion of a vinyl acetate polymer (exactly, a polymer in which a copolymer of vinyl alcohol and vinyl acetate is formed), and polymers obtained by saponifying a trifluorovinylacetate polymer, a vinyl formate polymer, a vinyl pivalate polymer, a tert-butylvinylether polymer, a trimethylsilylvinylether polymer, and the like (the details of "polyvinyl alcohol" can be referred to, for example, "World of PVA", Edited by the Poval Society and Published by Kobunshi Kankoukai, Japan, 1992 and "Poval", Edited by Nagano et al. and Published by Kobunshi Kankoukai, Japan, 1981). The degree of saponification in polyvinyl alcohol is preferably 70 mole % or more, more preferably 85 mole % or more, particularly preferably 98 mole % or more, that is, so-called perfect saponification. The degree of polymerization of polyvinyl alcohol is preferably 100 to 5,000, more preferably 200 to 3,000.

The term "polysaccharide" used herein means biopolymers which are synthesized by condensation-polymerization of various monosaccharides in a living body, and includes chemically modified biopolymers. The polysaccharides include, for example, cellulose; cellulose derivatives such as hydroxymethylcellulose, hydroxyethylcellulose, carboxymethylcellulose and the like; amylose; amylopectin; pluran; cardran; xanthan; chitin; chitosan and the like.

In this invention, a cross-linking agent for the hydrogen-bonding group may be used for the purpose of improving the barrier properties of the resin after water-resistant environmental test.

The cross-linking agent for hydrogen-bonding group is not critical, and includes, for example, titanium coupling agent, silane coupling agent, melamine coupling agent, epoxy coupling agent, isocyanate coupling agent, copper compound, zirconium-containing compound and the like, and preferable is the zirconium-containing compound.

Specific examples of the zirconium-containing compound include, for example, zirconium halides such as zirconium oxychloride, zirconium hydroxychloride, zirconium tetrachloride, zirconium bromide and the like; zirconium salts with mineral acids such as zirconium sulfate, basic zirconium sulfate, zirconium nitrate and the like; zirconium salts with organic acids such as zirconium formate, zirconium acetate, zirconium propionate, zirconium caprylate, zirconium stearate and the like; zirconium complexes such as ammonium zirconium carbonate, sodium zirconium sulfate, ammonium zirconium acetate, sodium zirconium oxalate, sodium zirconium citrate, ammonium zirconium citrate and the like; etc.

The amount of the cross-linking agent for hydrogen-bonding group added is not particularly limited so long as

the ratio (K) of the number of moles (CN) of the cross-linking group of the cross-linking agent to the number of moles (HN) of the hydrogen-bonding group of the high hydrogen-bonding resin (namely, $K=CN/HN$) falls within the range of 0.001 to 10, and preferably within the range of 0.01 to 1.

The composition ratio (volume ratio) of the non-film-forming inorganic laminar compound to the high hydrogen-bonding resin used in this invention is generally in the range of 5/95-90/10, preferably in the range of 5/95-50/50.

When the volume ratio of the non-film-forming inorganic laminar compound is less than 5/95, the barrier properties are not sufficient, and when it is more than 90/10, the film-formability is not satisfactory.

The volume ratio can be calculated from the weight ratio of the inorganic laminar compound charged to the resin charged expressed by a fraction. Specifically, it can be calculated by dividing the numerator and the denominator of the fraction by the densities of the inorganic laminar compound charged and the resin charged, respectively. Generally, the density of a resin (for example, polyvinyl alcohol) sometimes varies with crystallinity of the resin, however, in the calculation of the volume ratio as mentioned above, it can be calculated, for example, on the assumption that crystallinity of polyvinyl alcohol is 50%.

The method of compounding the non-film-forming inorganic laminar compound with the high hydrogenbonding resin is not critical, and includes, for example, a method which comprises mixing a resin solution with a dispersion formed by previously swelling or cleaving the non-film-forming inorganic laminar compound with a solvent and then removing the solvent; a method which comprises adding a dispersion formed by swelling or cleaving the non-film-forming inorganic laminar compound with a solvent to the resin, and then removing the solvent, a method which comprises adding non-film-forming inorganic laminar compound to a solution dissolving a high hydrogen-bonding resin to form a dispersing solution containing a swollen and cloven non-film-forming inorganic laminar compound and removing a solvent from the solution, and a method which comprises heat-mixing the high hydrogen-bonding resin with the non-film-forming inorganic laminar compound. The former three are preferable since a particularly large aspect ratio is easily obtained.

In the above-mentioned former three methods, heat-ageing at a temperature of 110° C. to 220° C. after the removal of the solvent can enhance the water resistance of a film (the barrier properties after water-resistant environmental test). The ageing time is not critical, and it is necessary that the film temperature reaches at least the desired temperature. For example, in the case of contacting with a heating medium such as using a hot air drier, a period of 1 second to 100 minutes is preferred.

The heat source is not critical, and contact with hot roll, contact with a heating medium such as hot air or oil, heating with an infrared ray, heating with a microwave and other various means can be applied.

The effect of the water resistance referred to herein is remarkably high when the non-film-forming inorganic laminar compound is a non-film-forming clay mineral.

The resin composition of this invention is molded into various forms and then used. The form of the molded article is not critical, and when the molded article is used as a packaging material such as film, sheet, container (e.g. tray, bottle or the like), etc., gas barrier properties are sufficiently exhibited.

The molded article is usually used in the form of a laminate. The substrate of the laminate is not critical, and

general substrates such as resin, paper, aluminum foil, wood, woven fabric, non-woven fabric and the like may be used.

The resin to be used as a substrate includes polyolefin resins such as polyethylene (low density and high density), ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-hexene copolymer, ethylene-octene copolymer, polypropylene, ethylene-vinyl acetate copolymer, ethylene-methyl methacrylate copolymer, ionomer resin and the like; polyester resins such as polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate and the like; polyamide resins such as nylon-6, nylon-6,6, meta-xylenediamine-adipic acid condensation polymer, polymethyl methacrylimide and the like; acrylic resins such as polymethyl methacrylate and the like; styrene or acrylonitrile resins such as polystyrene, styrene-acrylonitrile copolymer, styrene-acrylonitrile-butadiene copolymer, polyacrylonitrile and the like; hydrophobized cellulose resins such as cellulose triacetate, cellulose diacetate and the like; halogen-containing resins such as polyvinyl chloride, polyvinylidene dichloride, polyvinylidene difluoride, Teflon and the like; hydrogen-bonding resins such as polyvinyl alcohol, ethylene-vinyl alcohol copolymer, cellulose derivatives and the like; engineering plastic resins such as polycarbonate resin, polysulfone resin, polyethersulfone resin, polyetheretherketone resin and the like; etc.

In the case of laminates in the form of a film, the outer layer is preferably a biaxially oriented polypropylene, polyethylene terephthalate or nylon film, a polyvinylidene dichloride-coated (so-called K-coat) biaxially oriented polypropylene, polyethylene terephthalate or nylon film or the like, and the inner layer is preferably a polyolefin resin film such as polyethylene (low density or high density) film, ethylene-propylene copolymer film, ethylene-butene copolymer film, ethylene-hexene copolymer film, ethylene-octene copolymer film, polypropylene film, ethylene-vinyl acetate copolymer film, ethylene-methyl methacrylate copolymer film or the like in view of good heat-sealability.

The method of laminating the resin composition of this invention to a substrate is not critical. When the substrate is a film or sheet, preferred is a coating method which comprises coating a coating solution of the resin composition on the surface of the substrate, drying the solution and then heat-treating the coated substrate or a method which comprises laminating the film of this invention to a substrate.

The coating method includes direct gravure method; reverse gravure method; microgravure method; roll-coating methods such as two-roll heat coat method, bottom-feeding three-roll reverse coat method and the like; doctor knife method; die coat method; dip coat method; bar coating method and combinations thereof.

The coating layer thickness may be varied depending upon the kind of substrate and the desired barrier properties, and it is preferably 10 μm or less, more preferably 1 μm or less, in terms of dry thickness.

When it is 1 μm or less, the transparency of the laminate is greatly high. The resin composition, laminate, and laminated film of the present invention preferably have a transparency selected in view of convenience. The transparency is preferably 80% or more of the total light transmission at a wavelength of 500 μm , more preferably 85% or more, particularly preferably 90% or more. Such a transparency can be suitably measured by, for example, a commercially available spectrophotometer (self-spectrophotometer, type 330, manufactured by Hitachi, Ltd.).

There is no lower limit, and the thickness is preferably 1 nm or more, more preferably 10 nm or more, particularly preferably 100 nm or more, in order to obtain effective gas barrier properties.

As far as the effect of this invention is not lost, the resin composition of this invention may contain various additives such as ultraviolet absorber, coloring matter, antioxidant and the like. This invention covers a laminated film and laminate which have at least one layer of the above-mentioned film.

According to this invention, it becomes possible to obtain a gas barrier film having high levels of gas barrier and moisture barrier properties not obtained from conventional films. This is achieved by using a non-film-forming inorganic laminar compound having a particle size of 5 μm or less and an aspect ratio of 50–5,000 in a mixture of a high hydrogen-bonding resin and a non-film-forming inorganic laminar compound.

As stated in Examples which appear hereinafter, when the non-film-forming inorganic laminar compound is not contained, the barrier properties are greatly inferior to this invention even if the same resin is used (see, for example, Example 1 and Comparative Example 1). Even if the resin composition is composed of a high hydrogen-bonding resin and an inorganic laminar compound, when the inorganic laminar compound has an aspect ratio of about 30, the barrier properties are inferior 100 times or more to the Examples of this invention (see, for example, Comparative Example 3 and Example 1). In the Examples, the barrier properties are greatly different between the case of an aspect ratio of about 100 and the case of an aspect of about 500, and the barrier-imparting effect is greatly changed at an aspect ratio of about 200. When the aspect ratio is more than 200, a greater barrier-enhancing effect can be expected.

In the process for forming a film by adding to a resin or a resin solution a dispersion formed by swelling or cleaving a non-film-forming inorganic laminar compound with a solvent and removing the solvent, heat-aging after the removal of the solvent (for example, at 150° C. for 10 minutes) greatly enhances the barrier properties of the film after water-resistant environmental test as compared with the case in which no heat-aging is effected. This means that when the film is used in packaging foods, the package is resistant to high temperature and moisture conditions, boiling treatment or retort treatment, and the film is very much useful in practice.

Moreover, the addition of a cross-linking agent for the hydrogen-bonding group (ammonium zirconium carbonate is used in this case) greatly enhances the barrier properties of the film after water-resistant environmental test. When this is combined with the above-mentioned heat-aging treatment, the effect is further increased, and the resulting film is more preferably used in packaging foods which may be subjected to high temperature and moisture conditions, boiling treatment or retort treatment.

The resin composition of this invention has so high level barrier properties as not to be predicted from conventional resin materials. The oxygen-permeability per μm of thickness of the film of this invention is not more than 2 cc/m²/day/atm, or in some cases not more than 0.2 cc/m²/day/atm, under the conditions that the temperature is 31° C. and the relative humidity is 61%, while even the ethylene-vinyl alcohol copolymer which has the best oxygen barrier properties among commercially available resins has an oxygen-permeability of 15 cc/m²/day/atm. Further, the ethylene-vinylalcohol copolymer remarkably deteriorates in its gas barrier property at high humidity exceeding 90% RH. As shown in Comparative Examples 25 and 26, its oxygen-permeability per μm exceeds 90 cc/m²/day/atm at a condition of 23.8° C., 94.5% RH. On the other hand, according to Examples 34–45, especially Example 45 of the present invention, oxygen-permeability per μm under the same

condition as above is 0.06 cc/m²/day/atm. This fact indicates that a film of the present invention has a very superior gas barrier property even at high humidity. The resin composition of this invention is greatly superior in barrier properties to conventional resins and is close to metal and ceramic in respect of barrier properties. Therefore, the resin composition can be used in uses requiring a metal such as aluminum foil or an inorganic material such as glass in view of gas barrier of the composition. Thus, the resin composition of this invention can be said to be a material which has broken down the common knowledge of gas barrier resin composition (such weak points of metal and ceramic that the former is opaque and the latter is brittle can be overcome by the resin composition of this invention).

That is to say, the resin composition of this invention can be used in the form of a film in packaging miso, sliced dried bonito, confectionery, noodle, ham, sausage, boiled rice, curry, stew and the like; in the form of a bottle as a squeeze bottle for mayonnaise or a container for juice, soy source, source, edible oil and the like; and can further be used for packaging industrial materials in medical, electronic, chemical and mechanical fields such as blood transfusion pack, semiconductor package, oxidative chemicals package, precision parts package and the like. Thus, the resin composition of this invention can be used in various forms in a wide field.

This invention is explained in more detail below referring to Examples; however, this invention is not limited to these Examples.

Various physical properties were measured by the following methods.

[Oxygen-permeability]

Measured by an oxygen-permeability measuring apparatus (OX-TRAN 10/50A manufactured by MOCON) at a temperature of 31° C. (moisture-controlling constant temperature bath: 21° C.) (the relative humidity was 61%).

[Thickness]

Measured by means of a digital thickness meter when the thickness is 0.5 μm or more or by means of a gravimetric analysis (the measured weight of a film having a unit area is divided by the area and then divided by the specific density of the composition) when the thickness is less than 0.5 μm, or by an elemental analysis in the case of a laminate of the resin composition of this invention to a substrate (the ratio of the thickness of the resin composition layer to the thickness of the substrate is determined from the ratio of the analysis value of the specific inorganic element (resulting from the composition layer) of the laminate to the analysis value of the specific element of inorganic laminar compound alone).

[Particle size]

Measured by an ultrafine particle size analyzer (BI-90 manufactured by Brookhaven) at a temperature of 25° C. in an aqueous solvent. The center diameter determined from the photon correlation method according to a dynamic light-scattering method is taken as particle size L.

[Aspect ratio calculation]

Using an X-ray diffractometry (XD-5A manufactured by Shimadzu Seisakusho), the inorganic laminar compound alone and the resin composition were subjected to diffraction measurement by a powder method to determine the spacing a (unit thickness) of the inorganic laminar compound, and it was confirmed from the diffraction measurement of the resin composition that there was a portion in which the spacing of the inorganic laminar compound was broadened. Using the particle size L determined by the above-mentioned method, the aspect ratio Z was determined from the equation $Z=L/a$.

EXAMPLE 1

Synthetic mica [terasilic mica (Na-Ts) manufactured by Topy Kogyo] was dispersed in ion-exchanged water (0.7 μS/cm or less) in a proportion of 0.65 % by weight. This dispersion is used hereinafter as a non-film-forming inorganic laminar compound dispersion (Liquid A). The particle size of the synthetic mica (Na-Ts) was 977 nm, and the a value obtained from the powder X-ray diffraction was 0.9557 nm, and the aspect ratio Z was 1043. Polyvinyl alcohol (PVA 210 manufactured by Kuraray, saponification degree: 88.5%, polymerization degree: 1,000) was dissolved in deionized water (0.7 μS/cm or less) in a concentration of 0.325% by weight. The resulting solution is used hereinafter as a high hydrogen-bonding resin solution (Liquid B). Liquid A and Liquid B were mixed so that the solid component ratio (volume ratio) [non-film-forming inorganic laminar compound/high hydrogen-bonding resin] was 3/7. The resulting mixture is used hereinafter as a coating solution. The coating solution was applied onto a substrate obtained by subjecting a triacetylcellulose (TAC) film (FUJITAC CLEAR manufactured by Fuji Photo Film Co., Ltd.) having a thickness of 76 μm to surface saponification treatment, and then dried at room temperature to obtain a gas barrier film. The dry thickness of the coating layer was 0.87 μm. The oxygen-permeability of the resulting laminated film at 31° C. and 61% RH was 0.092 cc/m²/day. This value was reduced to that in the case where the dry coating thickness was 1.0 μm to obtain an oxygen-permeability at 31° C. and 61% RH of 0.08 cc/m²/day. Hence, the laminated film was excellent in gas barrier properties.

EXAMPLE 2

The same procedure as in Example 1 was repeated, except that the high hydrogen-bonding resin of Liquid B was replaced with hydroxyethylcellulose (manufactured by Wako Junyaku Kogyo) to obtain a gas barrier film, which was then subjected to oxygen-permeability test. The result obtained is indicated in Table 1 which shows excellent gas barrier properties.

EXAMPLE 3

The same procedure as in Example 1 was repeated, except that the coating and drying were conducted using a direct gravure coater (Multicoater M-200 manufactured by Hirano Tech-Seed) by a direct gravure coating method (coating speed: 1.7 m/min, drying temperature: 80° C., repeatedly coated 4 times) to obtain a gas barrier film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates excellent gas barrier properties.

EXAMPLE 4

The same procedure as in Example 1 was repeated, except that a direct gravure coater (Multicoater M-200 manufactured by Hirano Tech-Seed) by a direct gravure coating method (coating speed: 1.7 m/minute, drying temperature: 80° C., repeatedly coated 4 times) and the substrate was replaced with a biaxially oriented polystyrene (OPS) film having a thickness of 25 μm [TYPE (TH) CO, corona-treated, manufactured by Asahi Chemical Industry Co., Ltd.] to obtain a gas barrier film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates excellent gas barrier properties.

COMPARATIVE EXAMPLE 1

The same procedure as in Example 1 was repeated, except that Liquid A was not used and a 1% by weight solution of

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polyvinyl alcohol (PVA 210 manufactured by Kurarey, saponification degree: 88.55%, polymerization degree: 1,000) in deionized water ($0.7 \mu\text{S}/\text{cm}$ or less) was substituted for the Liquid B, to obtain a film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates inferior gas barrier properties.

COMPARATIVE EXAMPLE 2

The same procedure as in Example 1 was repeated, except that Liquid A was not used and a 2% by weight solution of hydroxyethylcellulose (HEC manufactured by Wako Junyaku Kogyo) in deionized water ($0.7 \mu\text{S}/\text{cm}$ or less) was substituted for the Liquid B, to obtain a film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates inferior gas barrier properties.

COMPARATIVE EXAMPLE 3

The same procedure as in Example 1 was repeated, except that the Liquid A was replaced with a dispersion obtained by dispersing synthetic hectorite [Laponite XLG manufactured by Nihon Silica Kogyo, particle size: 35 nm, a value: about 1 nm (diffraction peak was broad), aspect ratio: about 35] in deionized water ($0.7 \mu\text{S}/\text{cm}$ or less) in a proportion of 2% by weight and the Liquid B was replaced with a 1% by weight solution of polyvinyl alcohol (PVA 210 manufactured by Kurarey, saponification degree: 88.5%, polymerization degree: 1,000) in deionized water ($0.7 \mu\text{S}/\text{cm}$ or less), to obtain a film, which was then subjected to oxygen-permeability test. The result obtained is shown in Table 1 which indicates inferior gas barrier properties.

COMPARATIVE EXAMPLE 4

The same procedure as in Example 1 was repeated, except that Liquid B was not used, to prepare a film. However, the synthetic mica was peeled off from the laminated film and flaws showed horribly on the film surface, and the film-formability was inferior.

COMPARATIVE EXAMPLE 5

Triacetylcellulose (TAC) film (thickens: $76 \mu\text{m}$, FUJITAC CLEAR manufactured by Fuji Photo Film Co., Ltd.) had an oxygen-permeability at 61% RH as shown in Table 1 which indicates greatly inferior gas barrier properties.

COMPARATIVE EXAMPLE 6

A biaxially oriented polystyrene (OPS) film having a thickness of $25 \mu\text{m}$ [TYPE (TH) CO, corona-treated, manufactured by Asahi Chemical Industry Co., Ltd.] had an oxygen-permeability at 31°C . and 61% RH as shown in Table 1 which indicates greatly inferior gas barrier properties.

EXAMPLES 5-15

The oxygen-permeabilities of films each composed of the non-film-forming inorganic laminar compound, high hydrogen-bonding resin and substrate shown in Table 2 in the proportions shown in Table 2 were measured. Each of the films was formed by coating on the substrate a coating solution consisting of Liquid A and Liquid B prepared in the same manner as in Example 1, except that both Liquids A and B had a concentration of 2% by weight, by a gravure coater (Testcoater NCR 3-230, CAG 150, CR3 manufactured by Yasui Seiki) by a microgravure coating method

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[coating speed: 1-3 m/minute, drying temperature: 60°C . (inlet heater) and 100°C . (outlet heater)]

The results obtained are shown in Table 2 which indicates excellent gas barrier properties.

COMPARATIVE EXAMPLES 7-13

The oxygen-permeabilities of films each composed of the inorganic laminar compound, resin and substrate shown in Table 2 in the proportions shown in Table 2 prepared in the same manner as in Examples 1-15 and the oxygen-permeability of the substrate alone were measured. The results obtained are shown in Table 2 which indicates inferior gas barrier properties.

EXAMPLES 16-25

Films each composed of the non-film-forming inorganic laminar compound, high hydrogen-bonding resin and substrate shown in Table 3 in the proportions shown in Table 3 which had been subjected to heat treatment after film-formation under the conditions shown in Table 3 were subjected to oxygen-permeability test before and after immersion in hot water. The films were prepared by coating the substrate with a coating solution prepared in the same manner as in Example 1, except that the concentrations of Liquids A and B were 2% by weight and a cross-linking agent for hydrogen-bonding group was added after the preparation of the coating solution consisting of Liquids A and B, by means of a gravure coater (Testcoater NCR 3-230, CAG 150, CR3 manufactured by Yasui Seiki) by a microgravure coating method [coating speed: 1-3 m/minute, drying temperature: 60°C . (inlet heater) and 100°C . (outlet heater)]. The heat treatment after film-formation was conducted by subjecting the films to treatment by a hot air dryer (Perfect Oven manufactured by Tabai Esupekku) at the predetermined temperature for the predetermined time. The oxygen-permeability test after immersion in hot water was conducted as follows: The sample was immersed in water at 60°C . for 13 hours, air dried, dried at 60°C . for 1 hour and then subjected to oxygen-permeability test.

The results obtained are shown in Table 3 which indicates excellent gas barrier properties. The films which had been heat-treated or films in which a cross-linking agent for the hydrogen-bonding group was used indicate remarkable enhancement of water resistance.

COMPARATIVE EXAMPLES 14-15

The oxygen-permeability test after immersion in hot water was conducted of films each composed of the inorganic laminar compound, resin, substrate and cross-linking agent shown in Table 3 in the proportions shown in Table 3, the films having been prepared by the same manner as in Examples 16-25 and heat-treated under the conditions shown in Table 3. The results obtained are shown in Table 3, which indicates inferior gas barrier properties and inferior water resistance.

EXAMPLES 26-33

Films each composed of the inorganic laminar compound, resin and cross-linking agent shown in Table 4 in the proportions shown in Table 4 which had been subjected to heat treatment after film-formation under the conditions shown in Table 4 were subjected to dissolution resistance test. The films were prepared by casting a coating solution prepared in the same manner as in Example 1, except that the concentrations of Liquids A and B were 2% by weight and

the cross-linking agent was added after the preparation of the coating solution consisting of Liquids A and B, on an acrylic resin plate so that the film thickness after drying became about 20 μm , and drying the resulting films at room temperature. The dissolution resistance test was conducted as follows: The film sample obtained was subjected to heat-treatment by a hot air dryer (Perfect Oven manufactured by Tabai Esupekku) at the predetermined temperature for the predetermined time, wrapped with a stainless steel net, immersed in hot water at 80° C. for 10 minutes, taken out together with the stainless steel net, air-dried and then air-dried at 60° C. for 1 hour, after which the weight percentage of the remainder was determined (the higher the percentage of remainder, the better the water resistance). The results obtained are shown in Table 4 which indicates excellent water resistance.

COMPARATIVE EXAMPLES 16-24

Dissolution resistance test was conducted of films each composed of the inorganic laminar compound, resin and cross-linking agent shown in Table 4 in the proportions shown in Table 4 prepared in the same manner as in Examples 26-33. The results obtained are shown in Table 4 which indicates inferior water resistance. In particular, in Comparative Example 19, coloration was violent; in Comparative Examples 21-23, deformation of film was violent; and in each case, the appearance was inferior.

EXAMPLES 34-45

Oxygen-permeability test was conducted in the same manner as in Examples 16-25, except that the test was conducted at high humidity. The results obtained are shown in Table 5 which indicate superior gas barrier property.

COMPARATIVE EXAMPLES 25 AND 26

Oxygen-permeability test was conducted at high humidity as in Examples 34-45 by using an ethylene-vinyl alcohol copolymer film (trade name: Eval EF-F, manufactured by Kuraray Co., Ltd., film thickness 15 gm) which is a commercially available barrier film. The results obtained are shown in Table 5 which indicate inferior gas barrier property.

COMPARATIVE EXAMPLES 27-29

A coated film solely composed of the inorganic laminar compound was laminated and the oxygen-permeability test was conducted in the same manner as in Comparative Example 4, except that a biaxially oriented polypropylene film (opp20) was used as the substrate, inorganic laminar compounds shown in Table 6 were used, and a concentration of the inorganic laminar compound dispersion (Liquid A) was 2% by weight.

All the results obtained indicate inferior gas barrier property and inferior film-formability.

TABLE 1

Resin composition									
		Kind of inorganic			Oxygen-permeability (cc/m ² /day/atm)				
Substrate	Kind of resin (C)	laminar compound (D)	Volume ratio D/C	Film thickness (nm)	Measurement conditions	Value found	Reduced value (composition thickness: 1 μm)	Remarks (appearance etc.)	
Example									
1	TAC76	PVA210	NaTs	3/7	870	31° C., 61% RH	0.092	0.08	
2	TAC76	HEC	NaTs	3/7	10000	31° C., 16% RH	0.185	1.85	
3	TAC76	PVA210	NaTs	3/7	28.4	31° C., 61% RH	5.94	0.16	
4	OPS25	PAV210	NaTs	3/7	24.3	31° C., 61% RH	2.13	0.05	
Comp. Ex.									
1	TAC76	PVA210	—	0/10	2000	31° C., 61% RH	240.6	481.2	
2	TAC76	HEC	—	0/10	10000	31° C., 61% RH	1829	18290	
3	TAC76	PVA210	Laponite	3/7	3200	31° C., 61% RH	4.72	15.1	
4	TAC76	—	NaTs	10/0	—	31° C., 61% RH	—	—	No film-formability
5	TAC76	—	—	—	—	31° C., 61% RH	833.3	—	Substrate film
6	OPS25	—	—	—	—	31° C., 61% RH	10284	—	Substrate film

TABLE 2

Example	Substrate	Resin composition				Film thickness (nm)	Oxygen-permeability (cc/m ² /day/atm)			Remarks (appearance etc.)
		Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Measurement conditions		Value found	Reduced value (composition thickness: 1 μm)		
5	OPET25	PVA117H	Kunipia F	1/9	348	31° C., 61% RH	0.17	0.06		
6	OPET25	PVA117H	"	2/8	554	31° C., 61% RH	0.05	0.027		
7	OPET25	PVA117H	"	3/7	587	31° C., 61% RH	<0.05	<0.029		

TABLE 2-continued

Resin composition								
Substrate	Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Film thickness (nm)	Measurement conditions	Oxygen-permeability (cc/m ² /day/atm)		Remarks (appearance etc.)
						Value found	Reduced value (composition thickness: 1 μ m)	
8	OPET25	PVA117H	"	5/5	594	31° C., 61% RH	0.05	0.029
9	OPET25	PVA110	Smecton SA	3/7	440	23° C., 78% RH	2.88	1.26
10	OPET25	PVA110	NaTs	3/7	120	23° C., 78% RH	0.92	0.11
11	OPET12	PVA103	Smecton SA	2/8	375	31° C., 61% RH	1.32	0.495
12	OPET12	PVA103	Kunipia F	2/8	335	31° C., 61% RH	0.20	0.067
13	ONy15	PVA117H	"	3/7	769	31° C., 61% RH	<0.05	<0.038
14	OPP20	PVA117H	"	2/8	506	31° C., 61% RH	0.06	0.03
15	OPET12	PVA124	"	2/8	525	31° C., 61% RH	0.24	0.13
Com. Ex.								
7	OPET25	PVA110	—	—	520	23° C., 78% RH	11.69	6.07
8	OPET12	PVA103	Laponite	2/8	362	31° C., 61% RH	4.48	3.62
9	ONy15	PVA117H	—	—	1450	31° C., 61% RH	2.74	3.97
10	OPET12	PVA124	—	—	1104	31° C., 61% RH	2.12	2.34
11	OPET12	—	—	—	—	31° C., 61% RH	155.6	—
12	ONy15	—	—	—	—	31° C., 61% RH	50.6	—
13	OPP20	—	—	—	—	20° C., 0% RH	1500	—

TABLE 3

TABLE 2										
Resin composition										
Substrate	Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Film thickness (nm)	Crosslinking	Heat-treating conditions	Hot-water immersion conditions	Oxygen-permeability (cc/m ² /day/atm)		
								Conditions	Value found	
Example										
16	OPET25	PVA117H	NaTs	3/7	382	—	—	31° C., 61% RH	0.09	
17	OPET25	PVA117H	NaTs	3/7	382	—	60° C., 13 hr	31° C., 61% RH	8.25	
18	OPET25	PVA117H	NaTs	3/7	382	—	100° C., 10 min	60° C., 13 hr	31° C., 61% RH	6.47
19	OPET25	PAV117H	NaTs	3/7	382	—	150° C., 10 min	60° C., 13 hr	31° C., 61% RH	0.46
20	OPET25	PVA117H	NaTs	3/7	382	—	180° C., 10 min	60° C., 13 hr	31° C., 61% RH	0.37
21	OPET25	PVA117H	NaTs	3/7	572	AZC	—	31° C., 61% RH	<0.05	
22	OPET25	PVA117H	NaTs	3/7	572	AZC	—	60° C., 13 hr	31° C., 61% RH	0.28
23	OPET25	PVA117H	NaTs	3/7	572	AZC	100° C., 10 min	60° C., 13 hr	31° C., 61% RH	0.09
24	OPET25	PVA117H	NaTs	3/7	572	AZC	150° C., 10 min	60° C., 13 hr	31° C., 61% RH	0.05
25	OPET25	PAV117H	NaTs	3/7	572	AZC	180° C., 10 min	60° C., 13 hr	31° C., 61% RH	<0.05
Comp. Ex.										
14	OPET25	PVA117H	—	0/10	263	—	—	60° C., 13 hr	31° C., 61% RH	63.06
15	OPET25	PVA117H	—	0/10	263	—	180° C., 10 min	60° C., 13 hr	31° C., 61% RH	32.82

TABLE 4

Resin composition							
Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Crosslinking agent	Film thickness (μ m)	Dissolution resistance test (Hot water immersion: 80° C., 10 min)		Remarks (Appearance, etc.)
					Heat-treating conditions	Weight percentage of remainder (wt %)	
Example							
26	PVA117H	Kunipia F	3/7	—	20	80° C., 10 min	80.0
27	PVA117H	"	3/7	—	20	100° C., 10 min	80.4
28	PVA117H	"	3/7	—	20	150° C., 10 min	92.1
29	PAV117H	"	3/7	—	20	180° C., 10 min	96.6
30	PVA117H	"	3/7	AZC	20	80° C., 10 min	91.9
31	PVA117H	"	3/7	AZC	20	100° C., 10 min	93.7

TABLE 4-continued

Resin composition						Dissolution resistance test (Hot water immersion: 80° C., 10 min)		
	Kind of resin (C)	Kind of inorganic laminar compound (D)	Volume ratio D/C	Crosslinking agent	Film thickness (μ m)	Heat-treating conditions	Weight percentage of remainder (wt %)	Remarks (Appearance, etc.)
	32	PVA117H	"	3/7	AZC	20	150° C., 10 min	98.7
	33	PVA117H	"	3/7	AZC	20	180° C., 10 min	100
Comp. Ex.								
	16	PVA117H	—	0/10	—	20	—	0 (Completely dissolved)
	17	PVA117H	—	0/10	—	20	80° C., 10 min	0 (Completely dissolved)
	18	PVA117H	—	0/10	—	20	100° C., 10 min	0 (Completely dissolved)
	19	PAV117H	—	0/10	—	20	150° C., 10 min	0 (Completely dissolved)
	20	PVA117H	—	0/10	—	20	180° C., 10 min	81.3
	21	PVA117H	—	0/10	AZC	20	80° C., 10 min	77.6
	22	PVA117H	—	0/10	AZC	20	100° C., 10 min	88.1
	23	PVA117H	—	0/10	AZC	20	150° C., 10 min	97.9
	24	PVA117H	—	0/10	AZC	20	180° C., 10 min	96.5

Note to Tables 1 to 4:

Substrate

TAC76: Triacetylcellulose (trade name: FUJITAC CLEAR, manufactured by Fuji Photo Film Co., Ltd.), surface-saponified product, film thickness: 76 μ mOPS25: Biaxially oriented polystyrene film (trade name: Styrofilm (TH)CO, manufactured by Asahi Chemical Industry Co., Ltd.), corona-treated on one side, film thickness: 25 μ mOPET25: Biaxially oriented polyethylene terephthalate film (trade name: Lumilar, manufactured by Toray Industries, Inc.), corona-treated on one side, film thickness: 25 μ mOPET12: Biaxially oriented polyethylene terephthalate film (trade name: Lumilar, manufactured by Toray Industries, Inc.), corona-treated on one side, film thickness: 12 μ mONy15: Biaxially oriented nylon film (trade name: Emblem ON, manufactured by Unitika Ltd.), corona-treated on one side, film thickness: 15 μ mOPP20: Biaxially oriented polypropylene film (trade name: Pyren Film-OT, manufactured by Toyobo Co., Ltd.), corona-treated on one side, film thickness: 20 μ m

Resin

PVA210: Polyvinyl alcohol (trade name: Poval 210, manufactured by Kuraray Co., Ltd.), saponification degree: 88.5 mole %, polymerization degree: 1,000

HEC: Hydroxyethylcellulose (manufactured by Wako Junyaku Kogyo)

PVA117H: Polyvinyl alcohol (trade name: Poval 117H, manufactured by Kuraray Co., Ltd.), saponification degree: 99.6 mole %, polymerization degree: 1,700

PVA110: Polyvinyl alcohol (trade name: Poval 110, manufactured by Kuraray Co., Ltd.), saponification degree: 98.5%, polymerization degree: 1,000

PVA103: Polyvinyl alcohol (trade name: Poval 103, manufactured by Kuraray Co., Ltd.), saponification degree: 98.5%, polymerization degree: 300

PVA124: Polyvinyl alcohol (trade name: Poval 124, manufactured by Kuraray Co., Ltd.), saponification degree: 98.5%, polymerization degree: 2,400

Inorganic laminar compound

NaTs: Synthetic tetrasilic mica (trade name: NaTs, manufactured by Topy Kogyo), particle size: 977 nm, a value: 0.9557 nm, aspect ratio: 1043

Laponite: Synthetic hectorite (trade name: Laponite XLG, manufactured by Nippon Silica Kogyo), particle size: 35 nm, a value: about 1 nm (diffraction peak: broad), aspect ratio: about 35

KunipiaF: High purity montmorillonite (trade name: KunipiaF, manufactured by Kunimine Kogyo), particle size: 560 nm, a value: 1.2156 nm, aspect ratio: 461

SmectonSA: Synthetic saponite (trade name: SmectonSA, manufactured by Kunimine Kogyo), particle size: 108 nm, a value: about 1 nm (diffraction peak: broad), aspect ratio: about 108

Cross-linking agent

AZC: Ammonium zirconium carbonate (trade name: ZircosolAC-7, manufactured by Daiichi Kigenso Kogyo), aqueous solution containing 15% by weight of zirconium oxide, added so that the amount of hydrogen-bonding group in the resin became 15 moles per mole of zirconium element.

TABLE 5

Oxygen-permeability (cc/m ² /day/atm)					
Sample	Heat-treating conditions	Measurement conditions	Value found	Reduced value per μ m	
Example					
34	Example 16	—	23.9° C., 90.8% RH	0.37	0.14
35	"	150° C., 10 min	"	0.41	0.16
36	"	180° C., 10 min	"	0.21	0.10
37	Example 21	—	"	0.36	0.20
38	"	150° C., 10 min	"	0.13	0.07

TABLE 5-continued

		Oxygen-permeability (cc/m ² /day/atm)			
Sample	Heat-treating conditions	Measurement conditions	Value found	Reduced value per μm	
39	"	180° C., 10 min	"	0.10	0.06
40	Example 16	—	23.8° C., 94.5% RH	1.01	0.38
41	"	150° C., 10 min	"	0.80	0.30
42	"	180° C., 10 min	"	0.66	0.25
43	Example 21	—	"	0.65	0.37
44	"	150° C., 10 min	"	0.18	0.10
45	"	180° C., 10 min	"	0.11	0.06
Comp. Ex.					
25	EVOH-F	—	23.9° C., 90.8% RH	5.0	75
26	"	—	23.8° C., 94.5% RH	6.5	97.5

EVOH-F: Ethylene-vinylalcohol copolymer (trade name, Eval-EF-F, mfd. by Kuraray Co., Ltd.; thickness 15 μm)

TABLE 6

		Oxygen-permeability		
Kind of inorganic laminar compound [Thickness of the dried layer]	Value found (cc/m ² /day/atm)	Product of Thickness of the dried layer and Value found (cc. μm /m ² /day/atm)	Remarks (appearance, etc.)	
Comp. NaTs	2000	1000	Blanching	
Ex. 27 [5 μm]				
Ex. 28 Kunipia F [7 μm]	550	3850	Blanching	
Ex. 29 Smecton SA [20 μm]	1050	21000	A little opaque white	

What is claimed is:

1. A process for producing a resin composition or its film, said process comprising:

swelling or cleaving a non-film-forming inorganic laminar compound with a solvent to form dispersion;

mixing a resin or resin solution with the dispersion and thereby dispersing the non-film-forming inorganic laminar compound in the resin or resin solution; and

20 removing the solvent from the dispersion, if necessary in the form of a film, while maintaining the non-film-forming inorganic laminar compound in the swollen or cloven state.

25 2. The process according to claim 1, wherein the resin composition or film is subjected, after the removal of solvent, to heat-ageing further comprising heat-ageing the resin composition or its film at a temperature of 110° C. to 220° C., wherein said heat-ageing step is performed after said removing step.

30 3. The process according to claim 1, wherein the resin or resin solution contains a high hydrogen-bonding resin and a cross-linking agent reactive with a hydrogen bonding group of the hydrogen bonding resin, said process further comprising heat-ageing the resin composition or film at a temperature of 110° C. to 220° C., wherein said heat-ageing step is performed after said removing step.

35 4. The process according to claim 1, wherein the resin or resin solution comprises a high hydrogen-bonding resin and a zirconia compound as a cross-linking agent reactive with a hydrogen group of the hydrogen-bonding resin, said process further comprising heat-ageing the resin composition or film at a temperature of 110° C. to 220° C., wherein said heat-ageing step is performed after said removing step.

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